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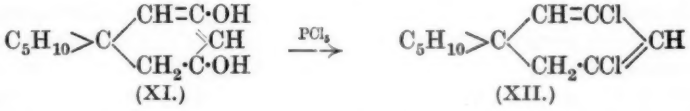
Action of Phosphorus Pentachloride on the spiro-*Diketone* (I). cyclo*Hexane*spiro-3 : 5-*dichloro*-$\Delta^{2:4}$-cyclo*hexadiene*.—After it had been found that the conversion of the *spiro*-alcohol into the corresponding halogen derivatives could not be carried out quantitatively, it was hoped that an increased yield of the final product might be obtained by eliminating both oxygen atoms from the molecule at an early stage of the reduction. Accordingly the action of phosphorus pentachloride on the diketone was investigated, in the hope that the latter might react in the dienol form (XI) to give the dichloro-unsaturated hydrocarbon (XII); an expectation which has been realised.



(XI.) (XII.)

The diketone (50 g.) was suspended in 130 c.c. of dry chloroform in a flask attached to a reflux apparatus; 125 g. of phosphorus pentachloride were gradually added in small quantities; after each addition the liquid boiled vigorously. The whole was heated for 3 hours on the water-bath, the cooled liquid filtered, and the chloroform distilled off. The residue was shaken well with ice-cold water, and the organic material taken up in ether. The ethereal solution, after being well washed with a dilute solution of caustic soda and then with water, was dried over calcium chloride. The residue after removal of the ether was distilled under reduced pressure. Only a very little impure diketone was recovered from the alkaline washings. cyclo*Hexane*spiro-3 : 5-*dichloro*-$\Delta^{2:4}$-cyclo*hexadiene* was thus obtained (yield 65%) as a pale yellow oil, b. p. 152°/21 mm. (Found : Cl, 32·5. $C_{11}H_{14}Cl_2$ requires Cl, 32·7%).

Unfortunately it has not yet been possible, by the use either of acid or of alkaline reducing agents, to prepare from this material a pure compound free from halogen.

This work was carried out at the Imperial College of Science and Technology under the direction of Professor J. F. Thorpe, C.B.E., F.R.S., to whom the author is grateful for kind help and encouragement. His thanks are also due to the Department of Scientific and Industrial Research and to the Chemical Society for grants which have made this research possible.

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XXXVII.—*The Interaction between Copper and Sulphuric Acid.*

By Cecil William Rogers.

The reactions which occur between copper and sulphuric acid have been investigated by Berzelius ("Traité de Chimie," IV, p. 324), Barruel (*J. Pharm.*, 1834, **20**, 13), Maumené (*Ann. Chim. Phys.*, 1846, **18**, 311), Calvert and Johnson (J., 1866, **19**, 438), Pickering (J., 1878, **33**, 122), Baskerville (*J. Amer. Chem. Soc.*, 1895, **17**, 904), van Deventer (*Chem. Centr.*, 1905, **1**, 992), and Sluiter (*ibid.*, p. 903).

Berzelius noticed that a black residue formed during the reaction, which could be oxidised by nitric acid, and was of the opinion that it was the sub-sulphate. He made no analyses of the substance. Barruel found that the action could take place at the ordinary temperature if sufficient time was allowed. He held that sulphur dioxide was first formed which attacked the copper with the formation of cuprous sulphide and cupric oxide, the latter then dissolving in the excess of acid to form the sulphate. He also made no analyses of the supposed sub-sulphide. Maumené suggested that more than one reaction proceeds at the same time, and introduced the idea of two primary reactions with a number of secondary reactions. One of these primary reactions led to the formation of sulphur dioxide and cupric sulphate; the other to the production of cuprous sulphide as one resultant, which, in consequence of the secondary reactions, became oxidised through the stages Cu_2S; $CuO,2Cu_2S$; $CuO,2CuS$; CuO,CuS; to CuO. Calvert and Johnson carried out a few experiments on the relative effect of concentrated and dilute acid at temperatures between 130° and 150°. They observed the formation of cuprous sulphide, which they considered was due to free sulphur combining with the metal. They made no analyses, but gave the following reasons for their opinions: (1) No hydrogen sulphide is evolved, (2) no sulphur is volatilised, (3) the analogy between this reaction and that of sulphuric acid upon tin.

Pickering carried out a thorough examination of the subject in all its aspects and concluded that there were two primary reactions and two secondary reactions, the latter being dependent on the second primary reaction. He gave the following equations:

A. *Primary Reactions.*

(1) $Cu + 2H_2SO_4 = SO_2 + CuSO_4 + 2H_2O$,

which was supposed to depend on the formation of nascent hydrogen.

(2) $5Cu + 4H_2SO_4 = Cu_2S + 3CuSO_4 + 4H_2O$.

B. *Secondary Reactions.*

(1) $Cu_2S + 2H_2SO_4 = CuS + CuSO_4 + SO_2 + 2H_2O$.
(2) $CuS + 2H_2SO_4 = S + CuSO_4 + SO_2 + 2H_2O$.

He stated that the primary reactions may occur either alone or together; that the metal is attacked at all temperatures from 19° upwards, the extent of the action increasing with rise in temperature; that very little gas was observed below 130°, and none at all insoluble in water; and that a deposit of sulphur was formed in the neck of the vessel either before or after the complete dissolution of the metal. He showed that no hydrogen sulphide was evolved, and he was the first to point out that the black residue in the flask consisted solely of copper and sulphur in the proportions required by the formula Cu_2S. From his observation that the ratio of $Cu_2S/CuSO_4$, expressed in terms of the copper content, decreased with diminishing temperature, and that the maximum ratio obtainable in the case of the second primary reaction was 2 : 3, he attempted to ascertain the temperature at which this reaction should go on alone. In this he was not successful, although approximations were obtained with the concentrated acid at 80° and with dilute acid at 130°. In no case was a ratio greater than 2 : 3 observed. He gave a number of reasons to show that the sulphide could not be formed either by the action of nascent hydrogen, hydrogen sulphide, or by the direct action of free sulphur on the metal.

Baskerville also carried out a series of experiments in which most of his work was in accord with that of Pickering. He gave the same equations, but differed in the detail of the operation of the primary reactions. He held that the first primary reaction predominates at all temperatures between 0° and 270° and that the proportion of material conforming to the second primary reaction increases from 0° to 100°, and then decreases from 100° to 270°. Below 100°, the primary reactions alone take place, the secondary reactions becoming evident at the higher temperatures with prolonged action, although even then, with short time, evidence of the operation of only the primary reactions was found.

It is to be noticed that neither Pickering nor Baskerville took any account of the sulphur formed during the reactions beyond recording its formation and tracing its origin to the decomposition of the sulphides. They ignored altogether the possible influence it might have had on the results of their experiments, especially at the higher temperatures. Both are agreed that two primary reactions take place. The present work was undertaken to examine this question of two primary reactions, to discover reasons for the different views expressed upon their influence at various temper-

atures, and to ascertain the effect, if any, of the liberated sulphur upon the final result of the action.

Experimental.

The purest electrolytic copper foil obtainable and concentrated sulphuric acid (A.R.) were used. The foil was cut into pieces $3 \times 1{\cdot}6$ cm., one piece only being used in each experiment.

The apparatus consisted of a reaction tube, about 6 inches long, furnished with two tapped side tubes for the admission of an inert gas and the removal of the gaseous products, and a ground glass stopper from which the copper was suspended on a fine glass thread. Sufficient acid was employed to cover the metal completely when in the tube, the acid being maintained at the required temperature by means of a suitable bath for at least ½ hour before the introduction of the metal. A current of purified carbon dioxide was passed through the tube throughout an experiment, this creating an inert atmosphere, effectively removing the gaseous products, and keeping the surface of the metal fairly clean. The sulphur dioxide evolved, which was the only gaseous product of the reactions, was absorbed either by iodine or potassium permanganate. The amount of copper used was found by weighing the strip before and after an experiment, and the copper as sulphate was estimated as cupric oxide.

The Completed Action.—It is stated that at 270° the reaction represented by the equation

$$Cu + 2H_2SO_4 = SO_2 + CuSO_4 + 2H_2O$$

proceeds alone. A series of experiments carried out at 270° furnished evidence which, while supporting the above equation in so far as the final result is concerned, showed that this is not the only action which occurs. The complete conversion of the metal into the sulphate takes place within a few seconds of the introduction of the metal, and the gas is evolved with such rapidity that the copper is carried to the upper portion of the acid. Further, before the flood of gas commences, there is an appreciable interval, during which the surface of the metal becomes covered with a black deposit. This deposit is practically entirely acted upon at the conclusion of the experiment except for such very small particles as are carried out of the liquid by the upward rush of gas and deposited on the sides of the reaction vessel. The acid itself quickly assumes a blue colour and white crystals may be observed to fall continuously from the surface of the metal. The crystalline deposit at this temperature is always quite white and free from the grey tints found in that formed at lower temperatures. On examination under the microscope it is found to consist of a large number of imperfectly

formed crystals together with a few tabular crystals, the whole being characteristic of anhydrous copper sulphate when crystallised from the concentrated acid at the same temperature. The examination of the crystalline deposits obtained at different temperatures will be dealt with in a later section. The following results are typical of those obtained at this temperature :

No.	Cu used.	SO_2 found.	Cu as $CuSO_4$.	Cu as sulphide.	Sulphur.	Acid.
1	0·2692	0·2618	—	Trace	Trace	Slightly brown
2	0·4649	0·4333	—	,,	,,	Brown
3	0·4450	0·4208	—	,,	,,	Slightly brown
4	0·4920	0·4841	0·4820	,,	,,	,, ,,
5	0·4929	0·5016	0·4631	,,	,,	Red
6	0·5012	0·5126	—	None	None	Colourless

The sulphur dioxide was estimated by absorption in iodine solution and titration of the excess iodine by thiosulphate. The low values for the copper sulphate are due to the fact that the anhydrous salt was filtered off before analysis, the 2—3% of copper which remained in solution thereby being left out of account. That copper still remains dissolved in the acid may be shown by the addition of a saturated solution of potassium bromide, when a dark, amorphous precipitate of the anhydrous bromide is thrown down. The excess of sulphur dioxide in experiments (5) and (6) is probably due to the dissociation of the acid itself; both experiments were prolonged for some time after the action had ceased. The lower values in some of the other cases are due to incomplete collection of the total sulphur dioxide owing to the closure of the experiments within a few seconds of the cessation of the reaction.

An interesting point arises in connexion with experiment (5). After the action had ceased, the reaction tube and its contents were allowed to cool slowly during several hours, and the acid liquid was then bright red. The crystalline deposit was quite normal when viewed under the microscope, and the abnormal colour may be ascribed, perhaps, to the colloidal condition of traces of sulphur remaining in solution. This suggestion is supported by the fact that after several weeks the acid deposited a small quantity of sulphur and became brown; the sulphur redissolved on shaking, producing a reddish-brown solution. All attempts to reproduce this effect met with failure.

Since traces of both sulphur and sulphide were met with at 270°, the reaction temperature was raised, but in the majority of cases both persisted. This circumstance, together with the darkening of the metallic surface before the evolution of gas commences, points to the conclusion that the simple equation is not sufficient to explain the action even at this high temperature, and that the

formation of sulphide and the subsequent liberation of sulphur are probably steps in the series of reactions involved.

The Black Deposit.—The black deposit was therefore carefully investigated. Trial experiments showed that it is produced most abundantly between 100° and 130°. The material for examination was prepared by immersing a large piece of the metal in the acid, a current of carbon dioxide being passed continuously. When the metal became coated, it was removed and at once plunged into thoroughly boiled water, beneath which the deposit was removed. The metal, after thorough cleansing and drying, was then returned to the acid, these operations being repeated until sufficient material had accumulated. Although the temperature range is most favourable to the rapid formation of the sulphidic matter, it also happens that the acid reacts with it fairly quickly, so that the actual amount of material collected is comparatively small. At lower temperatures, the rate of reaction is too slow for the rapid collection of the sulphidic matter.

The deposit was transferred from the water to a small platinum funnel, thoroughly washed with boiled water, dried, and weighed. Any sulphur present was extracted with carbon disulphide. The material was then treated with hot, concentrated nitric acid until no further action took place, the residual sulphur being weighed. The sulphur was removed by ignition from the funnel, which was weighed once more as a check. The copper and the oxidised sulphur in the filtrate from the nitric acid treatment were then estimated as cupric oxide and barium sulphate, respectively.

A large number of analyses of this type were carried out, and in every case the total percentage of copper and sulphur was about 100. There can be little doubt that the black residue consists entirely of copper and sulphur. The ratio of copper to sulphur, however, varied considerably, even in specimens collected from the same piece of metal and the same acid for different analyses; but the proportions always exhibited values between those required for cuprous sulphide and cupric sulphide, being nearer to the former than to the latter. It appears, therefore, that the first product is cuprous sulphide, which is then decomposed partly into cupric sulphide. The following table shows results obtained by the method of analysis given above :

Temp.	Cu %.	S %.	Total %.
100°	78·72	21·49	100·21
110	75·44	25·32	100·76
110	77·43	22·11	99·54
120—125	72·54	30·36	103·20
125	73·77	25·67	99·44
132	78·29	21·56	99·85

Cu_2S requires Cu, 79·86; S, 20·14% and CuS requires Cu, 66·48; S, 33·52%. No oxysulphides were obtained in any of these experiments.

The Secondary Reactions.—Experiments were then carried out with the two sulphides prepared by ordinary laboratory methods with the object of ascertaining the mode of decomposition of these substances in contact with the concentrated acid. Cupric sulphide was allowed to react with the acid at the required temperature until all had disappeared. The sulphur dioxide evolved was absorbed by iodine solution. A current of carbon dioxide was passed to assist in the removal of the sulphur dioxide, and to provide an inert atmosphere. The crystalline deposit was examined microscopically and found to be characteristic of cupric sulphate, and to contain inclusions of undecomposed sulphide. For the estimation of the copper, both the crystalline deposit and the acid liquid were taken, since some sulphate remained in solution. The sulphur dioxide evolved was, in general, in excess of that required by the equation given below, the excess increasing up to a definite maximum with rise in temperature and with the duration of the experiment. This can only have been due to the sulphur set free during the reaction, some of which reacted with the acid, while some was volatilised and condensed in pale yellow crystals of the β-form on the cooler parts of the reaction tube. The volatile material, on being heated on a microscope slide covered by a small glass dome, underwent all the changes characteristic of the effect of heat on sulphur. Small portions heated with free access of air gave the unmistakable odour of sulphur dioxide and reduced potassium dichromate. From the data given in the table below, it is evident that the cupric sulphide reacts with the acid according to the equation.

$$CuS + 2H_2SO_4 = SO_2 + CuSO_4 + S + 2H_2O,$$

and that the sulphur reacts with more acid :

$$S + 2H_2SO_4 = 3SO_2 + 2H_2O.$$

Temp.	CuS used.	CuO as $CuSO_4$.	SO_2 found.	
100°	1·486 g.	1·225 g.	1·152 g.	
110	2·465	1·975	1·763	
120	2·613	2·142	2·435	
130	1·753	1·449	1·861	
140	3·792	3·097	3·471	
160	1·937	1·595	3·912	(prolonged action)
170	1·642	1·348	3·536	„ „

That cuprous sulphide reacts with sulphuric acid to produce cupric sulphide was established by the change of composition of the black sulphide after immersion in the acid for various periods, the acid being diluted considerably to stop the action. Sulphur

invariably made its appearance after a time. The experiments were made in pairs at different temperatures, one of each pair being stopped after a short time, the other carried on for some considerable time, especially at the lower temperatures, the rate of reaction being very slow. The original composition of the black sulphide was 79·81% Cu, 20·58% S in the two experiments at 60° and 79·82% Cu, 20·10% S in the others. The final compositions were :

Temp.	60°.	80°.	100°.	120°.	160°.
% Cu	75·71; 72·23	74·55; 69·64	76·82; 68·92	74·73; 68·51	76·22; 70·61
% S	24·18; 27·72	24·86; 30·02	22·81; 30·82	25·60; 30·72	23·51; 28·64

Sulphur dioxide was evolved continuously, but quantitative measurements were not made. Where a crystalline deposit was obtained, this was examined microscopically and found to be cupric sulphate. It thus appears that the cuprous sulphide decomposes into cupric sulphide with the simultaneous formation of cupric sulphate and sulphur dioxide according to the equation

$$Cu_2S + 2H_2SO_4 = CuS + CuSO_4 + SO_2 + 2H_2O,$$

and that the cupric sulphide so formed then reacts with the acid in the manner already described.

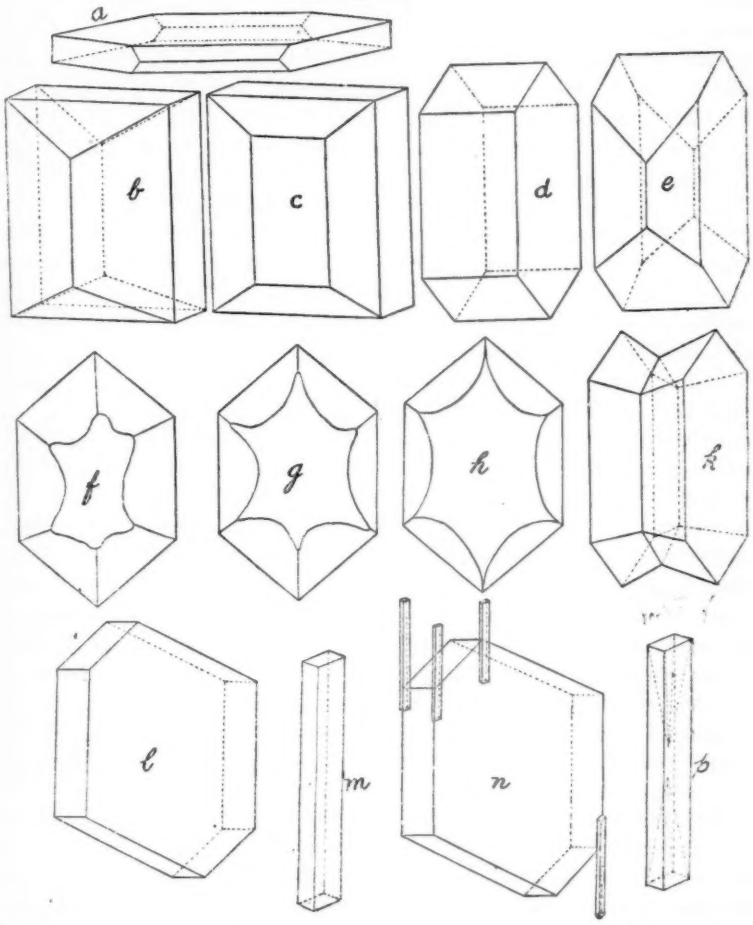
The Crystalline Deposit.—This has been stated by previous investigators to be anhydrous cupric sulphate, but as no means of identification were given, and owing to the possibility of the hydrolysis of a more complex substance on the addition of water, and the varying nature of some of the results obtained, it was thought necessary to examine the substance further. For this purpose the microscope was employed.

Except when prepared at the higher temperatures, above 200°, and even then, only when kept at this temperature for some time, under which conditions the substance is fairly soluble, producing a green solution, the deposit is never white ; it is generally of a dingy grey appearance. This is due to the fact that it contains a quantity of the two sulphides, the particles of which have served as nuclei round which the crystals have formed, thus protecting them from further attack by the acid. If such a deposit be treated with acid at a temperature higher than that at which it was formed, some of the crystals will dissolve, and the sulphides thus liberated will react with the acid in the usual manner. The employment of sufficient acid to dissolve the whole of the deposit results in the formation of a perfectly white, sulphide-free product on cooling.

At temperatures up to about 200° the crystalline deposit consists almost entirely of crystals belonging to the rhombic system, being combinations of the pinacoids, prism, and macrodome. Typical crystals are shown in the diagram (types a, b, c, d, and e). These

are transparent and colourless, and frequently contain inclusions of sulphide. Twinning is not of common occurrence except in the case of type a. There are, in addition to these rhombic crystals, others which appear to be monoclinic, are green, grouped, few in number, and are formed chiefly at 130° and above, at which

FIG. 1.



temperature the solution also is green. They might possibly be the acid sulphate.

At temperatures above 200° deposits of an entirely different character are obtained. The crystals are, for the most part, imperfectly developed, and of the rhombic crystals, only those of type d reach full development. Types a, b, c, and e are absent. Various

intermediate stages in the growth of type d may be found in abundance, the earlier stages being represented by crystals with one fully developed hexagonal face, partial development of the corresponding parallel face, growth being greatest in the regions opposite to the angles of the hexagon, these faces being united by six inclined planes (types f, g, h). Continued growth of the irregular face leads ultimately to the formation of a hexagonal face corresponding to that originally present, the two being now united by twelve inclined planes and presenting the appearance of k. Subsequent growth fills up the hollows to produce the perfect crystal. The mode of formation appears to resemble that of the crystals of the alkali halides. In addition to these imperfect forms, there are a large number of monoclinic crystals, tabular parallel to the ortho axis (l). These are well developed. On cooling the solution obtained at these temperatures, no further deposition of rhombic crystals takes place; instead, long slender prisms make their appearance below about 180° (m). The prisms grow either on the monoclinic crystals just mentioned, or singly, or, occasionally, in groups. They appear to belong to the triclinic system, although their arrangement parallel to the orthopinacoid when growing on the monoclinic plates suggests that they also might be monoclinic (n). Many of them are hollowed out from the position of the basal pinacoid faces inwards, presenting the appearance of p. Copper sulphate pentahydrate, specially prepared for the purpose, was dehydrated either by heat, or by immersion in concentrated sulphuric acid for some days. The anhydrous substance, prepared in either manner, in solution in the concentrated acid below 180°, deposits nothing but the prismatic crystals previously mentioned. If, however, the solution is prepared at, say, 160°, so that it will become saturated at a considerably lower temperature, and is then set aside out of contact with moisture, nothing deposits from it for some time, but when crystallisation does set in, the rhombic crystals are formed to the exclusion of the long, slender prisms. This process may require two or more days for its completion.

At temperatures above 200° the crystals obtained showed all the characteristics of those prepared by the action of the acid on the metal. It was found, further, that neither carbon dioxide nor sulphur dioxide exerted any influence on the type of crystal developed at any temperature, and that no sulphur dioxide was evolved on heating the crystals with the acid. There can be little doubt, therefore, that the crystalline deposit obtained by heating the acid with the metal is anhydrous cupric sulphate; moreover, it appears that the anhydrous salt is at least dimorphous, and possibly trimorphous.

The Primary Reaction.—Both Pickering and Baskerville were agreed that two primary reactions take place. It would seem rather unusual, however, for two substances to react in two totally different ways at the same temperature unless one of them be metameric. Of the reactants concerned, the acid is the only one which could fulfil this condition, and there is no evidence to show that it does actually exist in more than one form. Hence it is to be expected that only one primary reaction could take place. Further, both Pickering and Baskerville state that below 130° the evolution of gas is very slow, and that only at this temperature do bubbles of gas make their appearance. If the acid acted on the metal directly with the production of sulphur dioxide, it would be expected that bubbles of gas would be observable with ease at much lower temperatures, as in the case of zinc with dilute sulphuric acid. Even if the zinc and the acid be highly purified, the bubbles may be readily detected, although the action is slow. This again points to the possibility that the gas does not arise from the direct action of the acid on the metal, and that two primary reactions do not, in fact, take place.

If a piece of the purest electrolytic copper foil be totally immersed in the concentrated acid which has been heated to, and maintained at, a given temperature in an atmosphere of carbon dioxide for about ½ hour before the introduction of the metal, the following observations may be made :

At 50°. The first visible product of the interaction is a film on the metal, of a brownish hue, the formation of which is indicated by the loss of lustre of the metallic surface. This film gradually leaves the surface of the copper, the whole of which it covers, and it is then seen to be of almost the same shade as the metal itself. It remains suspended in the acid, being slowly moved about by the convection currents, and may be observed to change its colour to yellow and then to disappear—dissolve in the acid—colouring the latter yellow also. After this cycle of changes has proceeded for some time the acid becomes opalescent. No gas bubbles can be observed on the surface of the metal, yet sulphur dioxide is undoubtedly formed after a time.

At 50—120°. On increasing the initial temperature the formation of the brown material takes place with increasing rapidity, as also the conversion of this into the yellow substance. No gas bubbles can yet be observed.

At 130—140°. At about 130° the same phenomena occur with great rapidity, and at the same time bubbles of gas make their appearance; but no bubbles are formed until a deposition of the film has taken place. The particles constituting the film at this

temperature soon coalesce, the material then appearing black and forming a coating on the metal. The acid darkens owing to the suspended sulphide, but if the metal be removed it rapidly becomes clear again. Sulphur is deposited on the cooler parts of the apparatus.

The initial formation of the brown film could still be detected at temperatures above 140°. In every case there was an appreciable interval between the immersion of the metal and the appearance of the gas bubbles, which were never formed until the black sulphide had been produced. Hence the formation of sulphur dioxide is probably not due to the direct action between the acid and the metal. Support for this contention is found in the results of the following experiments.

A single piece of foil was totally immersed in the concentrated acid contained in one of the reaction tubes, the exit tube from which was connected by a series of T-pieces to absorption tubes in such a manner that any one of the latter could be put into communication with the reaction vessel directly, the change from one to another being made with the utmost facility. A current of carbon dioxide was passed throughout each experiment, the acid being heated to, and maintained at the required temperature for at least $\frac{1}{2}$ hour before the introduction of the metal. The sulphur dioxide evolved was absorbed in potassium permanganate.

Experiment 1. *At* 50°. Twenty c.c. of $N/50$-potassium permanganate were placed in each of three absorption tubes, each being connected in turn to the reaction vessel. Upon the removal of each tube 25 c.c. of 0·918 $N/50$-oxalic acid were added to its contents, and the volume of permanganate solution required for the titration of the excess of oxalic acid was measured. In all these experiments the reagents were delivered from over the same range of the burettes employed, this ensuring uniformity in the quantities of liquids taken. By blank tests it was found that 4·8 c.c. of the permanganate solution were required to titrate the excess of oxalic acid. The following results were obtained :

1.	Removed after the expt. had proceeded for					5	mins.	.....	4·8 c.c.
2.	„	„	„	„	„	17	„	.....	4·7 „
3.	„	„	„	„	„	30	„	.....	4·9 „

No film had yet formed.

Experiment 2. *At* 60°. The same piece of copper was employed with fresh acid, the remaining details conforming to those of Experiment 1.

1.	Removed after the expt. had proceeded for					5	mins.	.....	4·8 c.c.
2.	„	„	„	„	„	19	„	.....	4·9 „

The film had formed and was about to leave the surface of the copper.

Experiment 3. *At* 50°. The same piece of copper was used with fresh acid.

1. Removed after the expt. had proceeded for 5 mins. ..... 4·8 c.c.
2. „ „ „ „ „ 50 „ ..... 4·9 „

The film had just made its appearance.

3. Removed after the expt. had proceeded for 70 mins. ..... 4·9 c.c.
4. „ „ „ „ „ 100 „ ..... 5·0 „

These experiments, and others carried out in a similar manner, clearly indicated that the sulphur dioxide is not produced before the formation of the sulphide, but that after the formation of the latter the liberation of the gas commences. The varying time interval between the immersion of the metal and the appearance of the film is probably due to the nature of the metallic surface.

In order to test the above experiments and to gain additional evidence, another series was carried out with the solutions of permanganate and oxalic acid diluted to $N/200$, so that the oxalic acid became 0·918 $N/200$. The titrations were carried out in Nessler cylinders, the end-points being judged by comparison with similar cylinders containing known amounts of permanganate. By blank tests, it was found that 20 c.c. of permanganate with 25 c.c. of oxalic acid required 5·0 c.c. of permanganate to titrate the excess of oxalic acid.

Experiment 1. *At* 60°.

1. Removed after the acid had been heated for 45 minutes before the addition of the copper ..... 5·0 c.c.
2. Removed 10 minutes after the addition of the copper ..... 4·9 „
3. „ 36 „ „ „ „ „ ..... 5·2 „

Film formation first observed at this point.

4. Copper removed after 90 minutes' contact with the acid and the $KMnO_4$ allowed to absorb the SO_2 during a further 60 minutes at the same temperature ..... 11·05 „

Experiment 2. *At* 85°. Same piece of copper used with fresh acid.

1. Removed after the acid had been heated for 30 minutes before the addition of the copper ..... 5·0 c.c.
2. Removed 12 minutes after the addition of the copper ..... 4·8 „
3. „ 20 „ „ „ „ „ ..... 4·8 „

First indication of film formation.

4. Copper removed after 45 minutes' immersion, the $KMnO_4$ being allowed to absorb the total SO_2 during a period of 2 days (30 c.c. of $KMnO_4$ and 20 c.c. of oxalic acid being used in this case) ..... 7·2 „

These experiments again show that no sulphur dioxide is derived from the action before the film of sulphide has been formed, that no sulphur dioxide is derived from the acid itself at this temperature, and that the production of sulphur dioxide commences after the sulphide has formed.

There is, therefore, no justification for asserting that two primary reactions occur. For, if the first primary reaction of Pickering and Baskerville predominated at all temperatures, sulphur dioxide would be expected before the formation of the film, and if the second primary reaction took precedence, as asserted by Baskerville at the particular temperature of these experiments, no change should be observable in the sulphide film, and the gas evolved should first appear on the surface of the metal.

There is only one primary reaction, that one producing cuprous sulphide and cupric sulphate irrespective of the temperature at which the experiment is carried out, the sulphide then decomposing in the usual manner. The formation of the sulphur dioxide is thus dependent on the secondary reactions between the acid, the sulphides and the sulphur, the quantity actually formed being governed by the extent of occlusion of the sulphides by the sulphate, and the volatility of the sulphur in addition to the time and concentration factors.

The following experiments were made with the object of ascertaining the total production of sulphur dioxide at different temperatures, its amount being also expressed as a percentage of that theoretically obtainable from the simple equation

$$Cu + 2H_2SO_4 = SO_2 + CuSO_4 + 2H_2O.$$

The experiments were prolonged until all the sulphides had disappeared, and the sulphur had either reacted, volatilised, or remained practically inactive, and all the sulphur dioxide had been collected :

Temp.	Cu used.	SO_2 found.	Per cent.	Temp.	Cu used.	SO_2 found.	Per cent.
50°	0·0013	0·0009	69	140°	0·2146	0·1853	86
50	0·0011	0·0006	55	180	0·3621	0·3317	91
85	0·0052	0·0025	50	200	0·3165	0·2849	90
100	0·0131	0·0075	57	270	0·4920	0·4841	98
110	0·0163	0·0124	76	270	0·4450	0·4208	95
120	0·0251	0·0213	85				

It is clear that the percentage of sulphur dioxide increases with increase of temperature. So also does the rate of reaction between the sulphides, the sulphur, and the acid, so that these substances have less chance of being occluded or volatilised. As the temperature increases, they are acted upon more and more rapidly until,

in the region of 270°, they are removed practically as fast as they are formed. It is also evident that below 100° the sulphur must react with the acid very slowly, in fact it is sometimes possible to find quite large particles present in the liquid after several days. If the quantity of acid employed be sufficiently large to dissolve the whole of the sulphate produced, thus preventing occlusion, and the time of the experiment be prolonged, there seems no reason, other than the volatility of the sulphur, why results closely agreeing with the simple equation should not be obtained at any temperature at which appreciable action between the substances concerned takes place. In particular, over the range 130—200°, the sulphur is volatilised to an extent sufficient to allow its weight to be determined. The continuous removal of the sulphide makes impossible the direct determination of the quantitative relationships of the first reaction, but if an experiment be stopped at any point, and the cuprous sulphide and the sulphur dioxide be estimated, it is possible to obtain approximate values. From the consideration of the secondary reactions, it is known that 40% of the sulphur dioxide evolved in the completed reactions is due to the decomposition of the sulphides. If the corresponding amount of cuprous sulphide be calculated and this result be added to the sulphide actually found, the total must represent that portion of the copper which has either passed, or is passing through, the sulphide stage. The difference between this figure and the total copper used gives the amount of metal which would have been found as sulphate had no sulphide been decomposed. The ratio of copper as cuprous sulphide to copper as cupric sulphate then determines the action.

The following table shows the results of a number of experiments calculated in this manner :

Temp.	Cu used.	Cu as Cu_2S.	SO_2.	Cu as Cu_2S =40% of SO_2.	Total Cu as Cu_2S $=A$.	Residual Cu as $CuSO_4$ $=B$.	Ratio A/B.
16°	0·1176	0·0113	0·0513	0·0205	0·0318	0·0858	2/5·4
80	0·0280	0·0013	0·0215	0·0086	0·0099	0·0181	2/3·7
80—90	0·0235	0·0005	0·0216	0·0086	0·0091	0·0144	2/3·2
100	0·0135	0·0016	0·0092	0·0037	0·0053	0·0082	2/3·1
100	0·0417	0·0120	0·0084	0·0034	0·0154	0·0263	2/3·4
120	0·0431	0·0085	0·0200	0·0080	0·0165	0·0266	2/3·2
140	0·0526	0·0079	0·0288	0·0115	0·0194	0·0332	2/3·4
160	0·2167	0·0217	0·1473	0·0589	0·0806	0·1361	2/3·4
170	0·2483	0·0198	0·1926	0·0771	0·0969	0·1514	2/3·1
190	0·2936	0·0176	0·2387	0·0995	0·1131	0·1805	2/3·2
200	0·3137	0·0157	0·2585	0·1034	0·1191	0·1946	2/3·3
240	0·4361	0·0087	0·3972	0·1589	0·1676	0·2685	2/3·2

Making allowance for the comparative inactivity of the sulphur at 16° and for the volatilisation of the sulphur at the higher temperatures, both of which tend to lower the ratio, it is clear that the value

of Cu as Cuprous Sulphide/Cu as Cupric Sulphate approximates to 2/3. This is satisfied by the following equation :

$$5Cu + 4H_2SO_4 = Cu_2S + 3CuSO_4 + 4H_2O,$$

which is the second primary reaction of Pickering and Baskerville. If this equation be added to those given for the secondary reactions, the simple equation—the first primary of Pickering and Baskerville —is obtained.

It will now be evident why it was considered that one of the primary reactions proceeded alone at 270°. The various actions succeed one another so rapidly that there is little chance of any sulphide or sulphur escaping. Hence the quantity of sulphur dioxide evolved agrees closely with that required theoretically. Pickering's failure to determine the temperature at which his second primary reaction took place exclusively is also explained. It proceeds alone momentarily only, for as soon as a film of cuprous sulphide is formed it begins to react with the acid. The obstructive properties attributed to the compact deposit of sulphide on the surface of the metal are due not so much to the sulphide itself as to the layer of inert sulphate with which it soon becomes covered when the acid is saturated; for, if a further quantity of acid be added so as to reduce the concentration of the sulphate, and thereby allow some of that on the metal to dissolve, the action at once becomes vigorous again.

Summary.

It is shown by these experiments that :

1. There is only one primary reaction.

2. The sulphur produced exercises a considerable influence on the final results of the reaction, very much more than has been ascribed to it hitherto.

3. The white crystalline deposit is undoubtedly anhydrous cupric sulphate, and this substance is at least dimorphous.

4. At any temperature the completed reaction may be represented by the simple equation

$$Cu + 2H_2SO_4 = SO_2 + CuSO_4 + 2H_2O,$$

which is the sum of the equations

$$\begin{aligned}
5Cu + 4H_2SO_4 &= Cu_2S + 3CuSO_4 + 4H_2O, \\
Cu_2S + 2H_2SO_4 &= CuS + CuSO_4 + 2H_2O + SO_2, \\
CuS + 2H_2SO_4 &= CuSO_4 + 2H_2O + SO_2 + S, \\
S + 2H_2SO_4 &= 2H_2O + 3SO_2,
\end{aligned}$$

these representing the actual sequence of events, and which, in suitable combination, will yield an equation expressing the stage attained by the reactants at any particular moment during an interaction.

In conclusion, the author desires to acknowledge his indebtedness to the Research Fund Committee of the Chemical Society for a grant and the loan of apparatus that enabled this research to be carried out.

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XXXVIII.—*Hydrogen Electrode Studies of the Reactions between Solutions of Salts of Weak Metallic Bases and the Acetate, Oxalate, and Tartrate of Sodium, with a Note on the Effect of Dextrose on Zirconium Chloride Solution.*

By HUBERT THOMAS STANLEY BRITTON.

IT has been shown (this vol., p. 125) that in the reactions between certain metallic salts and the alkali-metal salts of very weak acids (chromic [second stage], boric, and carbonic), basic substances separate when the solutions attain the p_H at which the respective hydroxides are precipitated.

The present paper deals with the reactions of the sodium salts of moderately weak acids, weak at least in respect of one stage of ionisation, with solutions of salts of weak bases and of bases which form "soluble basic salts." Sodium tartrate was one of the salts selected, first because of the comparative weakness of the acid and secondly because it was thought that the titrations might give some insight into the nature of complex tartrate solutions. Titrations with the hydrogen electrode have also been made of zirconium chloride solutions containing dextrose and alkali, in order to study the function of the hydroxy-group in these complex solutions.

All the electrometric titrations now recorded were performed with the hydrogen and normal calomel electrodes described in J., **1924**, **125**, 1576; 1925, **127**, 2111.

I. *Sodium Acetate Titrations.*

As acetic acid has a small dissociation constant, $1{\cdot}8 \times 10^{-5}$, it was thought that the hydrion concentrations produced during some reactions would be so low that the p_H would not be attained at which the hydroxides are precipitated, and it was expected, therefore, that basic acetates would be obtained from solutions of salts of the weakest bases.

Zirconium.—A solution of zirconium oxychloride, $ZrOCl_2$, slowly yields a precipitate on treatment with sodium acetate, but no pre-

cipitate is produced if there has been added to the solution the quantity of hydrochloric acid corresponding with the formula $ZrCl_4$.

The solubility of freshly precipitated zirconium hydroxide in acetic acid is inconsiderable; and this is in accord with hydrogen-ion requirements, for zirconia is precipitated from chloride or sulphate solution (J., 1925, **127**, 2135, 2138) before the hydrion concentration has been reduced to 10^{-2}, which acetic acid can barely acquire even in concentrated solution. Also it is not surprising that the zirconium tetra-acetate prepared (Rosenheim and Hertzmann, *Ber.*, 1907, **40**, 810) by dissolving anhydrous zirconium chloride in boiling anhydrous acetic acid hydrolyses completely and rapidly in water.

FIG. 1.

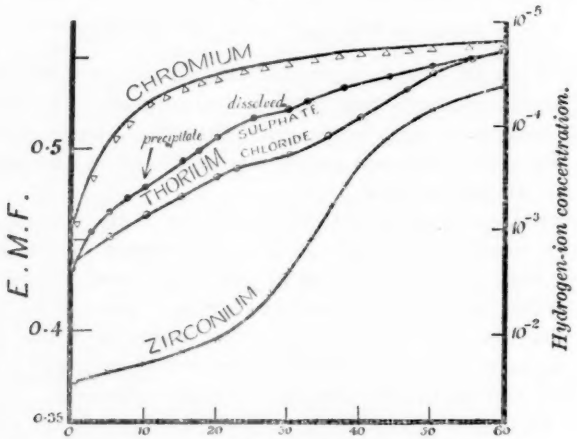


Fig. 1 shows the titration curve of 100 c.c. of $M/100$-zirconium chloride and $N/10$-sodium acetate at 18°. The solution remained clear throughout the titration. The extent to which the sodium acetate reacted with the zirconium chloride may be deduced from the hydrogen-ion concentrations of the solution when more than 40 c.c. (*i.e.*, 4 mols. of NaAc : 1 mol. of $ZrCl_4$) of sodium acetate had been added. These are in Table I, E being the *E.M.F.* of the hydrogen electrode measured against a N-calomel electrode.

TABLE I.

C.c. of $N/10$-NaAc.	E.	p_H.	p_H calc.
40	0·392	3·62	3·15
60	0·536	4·38	4·34
80	0·553	4·69	4·64
100	0·560	4·80	4·81

The values given in the last column were calculated on the assumption that no acetic acid had combined with the zirconium hydroxide, the reaction supposed to have taken place being $ZrCl_4 + 4NaAc + 4H_2O \rightarrow Zr(OH)_4 + 4HAc + 4NaCl$, and that the hydrogen-ion concentrations of the solution were due to the equilibria between these ions, the acetate ions from the sodium acetate (taken as 79% dissociated), and the acetic acid.

The agreement between the calculated and the observed values of p_H for additions of 60, 80, and 100 c.c. of sodium acetate seems to confirm the view that the solution, although quite clear, must have contained uncombined zirconium hydroxide. There is, however, no agreement between the values of p_H for the addition of 40 c.c. of sodium acetate; the higher, observed p_H is probably to be attributed to the presence of undecomposed sodium acetate, and not merely to the dissociation of all the acetic acid shown in the equation. It has been found from an acetic acid titration curve (see Prideaux, "Theory of Indicators," 1917, p. 226) that the observed value of p_H is 3·62 for an acetic acid solution which has been neutralised to the extent of 9% by sodium hydroxide. (In titrations of dilute solutions of weak acids the concentration of the solution has very little effect on the p_H ruling during the major part of the titration, the variations in p_H occurring at the beginning and the end.) In the zirconium titration, this proportion of acetic acid neutralised corresponds to 3·6 c.c. (*i.e.*, 9% of 40) of *N*/10-sodium acetate having remained unattacked, and therefore the reaction at this stage may be represented by the following scheme, 4 mols. of sodium acetate having been added to 1 mol. of zirconium chloride: $4NaAc + ZrCl_4 + 3{\cdot}64H_2O \rightarrow ZrCl_{0.36}(OH)_{3.64} + 3{\cdot}64HAc + 0{\cdot}36NaAc$. A highly basic zirconium chloride was therefore present in the solution. Its composition happens to be similar to that of the basic zirconium chloride, $ZrCl_{0.5}(OH)_{3.5}$, present during the greater part of the alkali titration of zirconium chloride solution (J., 1925, **127**, 2135).

The agreement of the observed with the calculated value of p_H obtained when an excess of sodium acetate had been added shows that the chloride which had earlier been attached to the zirconium hydroxide reacted with sodium acetate. It seems evident that the zirconium hydroxide was present in the solution in a colloidal state, although the solution was clear, probably owing to some slight solvent action of the acetic acid. Boiling brought about its slow decomposition.

The titrated solution was precipitable with alkalis, a precipitate first appearing when 1·2 equivalents of *N*/10-sodium hydroxide had been added.

Thorium.—Under certain conditions, sodium acetate produces a precipitate from thorium sulphate solutions, but not from those of thorium chloride. Two hydrogen electrode titrations were carried out, one of 100 c.c. of 0·01*M*-thorium chloride and the other of 100 c.c. of 0·01*M*-thorium sulphate, with *N*/10-sodium acetate. The curves are given in Fig. 1. Precipitation from the sulphate solution began when 10 c.c. of sodium acetate had been added and p_H 3·4 attained (the precipitation value of p_H is 3·5 for thorium hydroxide) and appeared to be at a maximum when 25 c.c. had been added, but after the addition of 30 c.c. the precipitate, which was chiefly basic sulphate, dissolved and a clear solution was obtained. No trace of a precipitate formed in the thorium chloride solution under these conditions. The two titration curves converged at 60 c.c. and then became coincident, at least during the addition of the next 40 c.c. of sodium acetate.

The changes in hydrogen-ion concentration which occurred after 60 c.c. of sodium acetate had been added are indicated by the data: 80 c.c., p_H 4·97; 100 c.c., p_H 5·15, and were such as would be caused by the presence of acetic acid in amounts varying from 1·5 to 1·9 equivalents per one atom of thorium. It appears, therefore, that the thorium hydroxide present in these solutions was associated with at least 2 equivalents of acetate radical. The fact that the solutions were quite clear, although the precipitation value of p_H, 3·5, for the hydroxide had been exceeded, seems to indicate that the thorium-ion concentration had become considerably reduced by the change which had taken place in the solution, a change which might have been due to the formation of complex ions, or, perhaps more probably, to the formation of basic thorium acetate micelles which were capable of undergoing a different kind of ionisation.

The precipitate Haber obtained by boiling a thorium chloride solution with sodium acetate (*Monatsh.*, 1897, **18**, 687) is interesting, in that it contained 2 equivalents of acetate to one atom of thorium.

The precipitation of basic thorium sulphate from thorium sulphate solutions by sodium acetate seems to be accounted for by the tendency of sulphates of weak bases to form fairly stable basic sulphates in solution (compare zirconium sulphate, J., 1925, **127**, 2140). The sodium acetate added to the 0·01*M*-thorium chloride solution had a continuous hydrolysing action, shown in the curve by the greater hydrogen-ion concentrations ruling during the early part of the reaction, whereas when it was added to the thorium sulphate solution hydrolysis was somewhat impeded, with the result that basic thorium sulphate was precipitated.

Acetic acid may have some solvent action on thorium hydroxide, for the hydrogen-ion concentrations of dilute solutions of the acid

are a little greater than that at which thorium hydroxide is normally precipitated (p_H 3·5). This solvent action may be responsible for the holding of thorium hydroxide in solution at a p_H greater than 3·5, by causing, through the formation of comparatively inert basic thorium acetate micelles, the concentration of thorium ions to be so reduced that the solubility product of thorium hydroxide is not exceeded.

Chromium.—Substances containing chromium and the acetate radical have been the subject of many investigations, chiefly by Weinland and his collaborators (see Weinland, "Einführung in der Chemie der Komplex-Verbindungen," Stuttgart, 1919). Their chief interest lies in the remarkable colour changes which they exhibit on becoming more and more basic; *e.g.*, the green solution of chromium acetate itself, on addition of alkali, may remain green or become red or reddish-violet according to conditions such as time of keeping or of boiling (compare Recoura, *Compt. rend.*, 1899, **129**, 158, 208). Weinland and Büttner (*Z. anorg. Chem.*, 1912, **75**, 293) claim that these colours are due to salts of one or more complex "acetato-chromium" bases, whose constitutions are supposed to be accounted for by the co-ordination theory. The fact that these so-called bases, although essentially basic substances, contain varying amounts of acetate, *viz.*, 2·67, 2·33, 2·17, 2, or 1·5 equivalents of acetate for each atom of chromium, suggests that the colours may be due to the basic acetates themselves, and this view is supported by the experiments now to be described.

The curve in Fig. 1 represents the titration of 100 c.c. of 0·01*M*-chrome alum with *N*/10-sodium acetate. The p_H, which was 4·80 when 60 c.c. of sodium acetate had been added, became, on addition of 100 c.c., 5·02, and only just fell short of the precipitation value (5·34) for the hydroxide. The failure of the sodium acetate to produce a higher p_H after the theoretical quantity (60 c.c.) had been added was due to the "buffering" effect of the liberated acetic acid. It was pointed out in previous papers that in salts of chromium with strong acids one equivalent of the acid radical is loosely bound and reacts with alkali-metal salts of weak acids as if it were free acid, liberating an equivalent quantity of weak acid. In the present titration, this would correspond to the setting free of 20 c.c. of *N*/10-acetic acid. An idea of the amount of acetic acid actually liberated may be obtained from the fact that the p_H produced on addition of 60 c.c. of sodium acetate was the same as that produced by neutralising 60% of the acid in *N*/10- or *N*/100-acetic acid with sodium hydroxide. It seems certain, therefore, that the solution, besides containing an appreciable amount of free acetic acid, contained also basic chromium acetate aggregates capable of supplying

acetate ions to the solution. The solution remained green throughout the titration and was precipitated by alkalis, but the precipitate redissolved on addition of less alkali than would have been necessary had the precipitate been obtained from a solution of a chromium salt of a strong acid.

Chromium combined with acetic acid sometimes resists precipitation by alkalis. This property depends on the treatment to which the solution has been subjected, as may be seen from the data in Table II: under *a* is the number of c.c. of *N*/10-sodium acetate that were added to 10 c.c. of *M*/10-chrome alum, and in the last two columns are the equivs. of *N*/10-sodium hydroxide (per 1 atom of chromium) that were required to produce (*b*) a precipitate and (*c*) neutrality to phenolphthalein.

TABLE II.

a.	Remarks.	Colour.	*b*.	*c*.
60	Violet chrome alum solution used, and mixed at room temperature.	Green.	0·64	2·81
„	Green chrome alum solution, mixed at room temperature.	„	1·18	2·67
„	Reactants mixed, boiled, and cooled to room temperature.	Purplish-green.	No ppte.	1·89
„	Alkali added to boiling reactants.	Green.	2·21	2·21 to 2·80
„	Reaction mixture on protracted boiling became completely precipitated as basic acetate.	Solution colourless.	—	2·51
„	Violet chrome alum; mixture kept for 24 hours.	Bluish-red.	1·76	2·38
120	„	Purple.	No ppte.; solution green.	2·11
„	Mixture boiled for 20 minutes and kept for 24 hours.	Green.	No ppte.	2·22

It will be noticed that in one case prolonged boiling caused basic chromium acetate to be precipitated completely; 2·51 equivs. of acetic acid remained in the solution, and therefore the composition of the precipitate was $CrAc_{0.49}(OH)_{2.51},xH_2O$. In three instances, solutions were obtained which were non-precipitable with sodium hydroxide; one of these, which contained a larger proportion of sodium acetate, was purple and had been rendered non-precipitable merely by keeping, the other two had been rendered so by initial boiling. The amounts of alkali required to make the three solutions alkaline to phenolphthalein, being approximately 2 equivalents to one atom of chromium, suggest that about 1 equivalent of acetate radical was linked to the chromium hydroxide in an inert manner,

probably in a colloidal complex. The reaction which took place while the chromium solution was thus changed by boiling may perhaps be represented by the following equation: $Cr_2(SO_4)_3 + 6NaAc + 2xH_2O = 2CrAc_{(3-x)}(OH)_x + 2xHAc + 3Na_2SO_4$. The data in the table show that the value of x in the basic complex, after any acid this may have set free by hydrolysis had been neutralised, varied from 1·89 to 2·22.

A further electrometric titration was carried out to ascertain whether the acid liberated in the formation of the basic complex was a complex acid or merely acetic acid. A mixture of 120 c.c. of N/10-sodium acetate with 10 c.c. of M/10-chrome alum was rendered non-precipitable by boiling for 5 minutes, and the reddish-violet solution cooled to 18°. The *E.M.F.* of the hydrogen electrode, compared with the N-calomel electrode, was 0·551 volt, and therefore p_H was 4·64. The first section of the curve representing the titration with N/10-sodium hydroxide was similar to that of acetic acid, and the free acid became neutralised when 46·8 c.c. of alkali had been added. The solution remained violet throughout the titration, but the violet solution to which 60 c.c. of N/10-sodium hydroxide had been added appeared colloidal after 24 hours, and was precipitated on continued boiling. If the basic acetate complex did not undergo any hydrolysis during the titration, the free acid was equivalent to 46·8 c.c. of N/10-acid and the excess of sodium acetate to 60 c.c. of N/10, 13·2 c.c. of N/10-sodium acetate having been decomposed. The sodium acetate being assumed to be 79% ionised, and the free acid to be acetic ($K = 1·8 \times 10^{-5}$), the hydrogen-ion concentration of the solution should have been $10^{-4·74}$, which is in fair agreement with the observed value. The experiment seems, therefore, to confirm the view expressed by the equation.

When the solution is rendered inert to alkalis merely by keeping, the hydrolysis is not so marked, and probably much of the acetic acid is in a state of loose combination. The change that renders the basic chromium acetate complex inert is probably similar to that which chromium hydroxide undergoes slowly on keeping, and rapidly on boiling, in contact with its mother-liquor. The hydroxide becomes considerably less reactive and requires an appreciable time for dissolution in acids. If the basic chromium acetate complexes are colloidal, they may undergo some ageing or stabilising process and their size may have some effect on the absorptive power for light which modifies the colour of the solution.

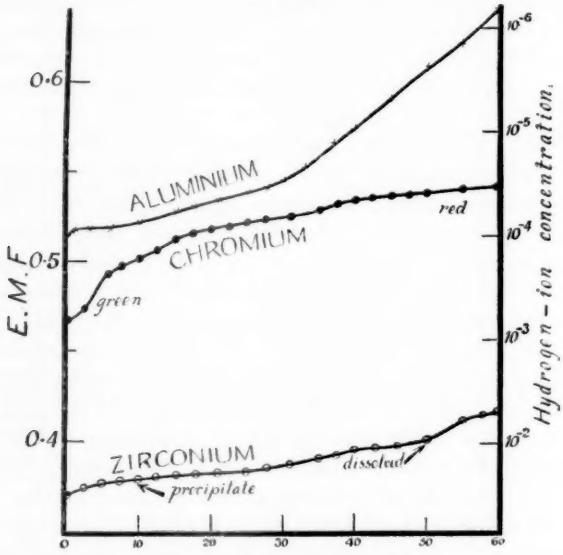
II. *Sodium Oxalate Titrations.*

Oxalic acid is a strong acid in regard to its first stage of ionisation, but fairly weak in respect to its second stage, K_2 being $1·3 \times 10^{-4}$

(J., 1925, **127**, 1905). The titrations described in this section were therefore carried out to see if the latter had any influence on the reactions between sodium oxalate and salts of weak bases. It is significant that the hydroxides which are generally supposed to enter into complex formation with oxalates are weak bases, all of which are precipitated by alkalis from solutions whose hydrion concentrations are greater than 10^{-7} (compare Schäfer and Abegg, *Z. anorg. Chem.*, 1906, **14**, 293).

Zirconium.—As zirconium hydroxide is ordinarily precipitated from solutions whose hydrogen-ion concentrations are greater than

FIG. 2.



10^{-2}, it was considered that the hydrogen-ions arising from the second dissociation of oxalic acid would be too few to affect the dissolution of the hydroxide.

The reaction between 100 c.c. of *M*/100-zirconium chloride and *N*/10-sodium oxalate was studied by means of the hydrogen electrode. The variation in hydrogen-ion concentration is given in Fig. 2. A gelatinous precipitate appeared when 10 c.c. of sodium oxalate had been added, and precipitation was at a maximum with 40 c.c., after which the precipitate began to dissolve; the solution became quite clear again on addition of 50 c.c. The precipitate obtained when 20 c.c. of sodium oxalate had been added had the composition $Zr(OH)_{2\cdot69}(C_2O_4)_{0\cdot69},xH_2O$. The precipitates obtained by Venable

and Baskerville (*J. Amer. Chem. Soc.*, 1897, **19**, 11) on treating zirconium chloride solutions with a saturated solution of oxalic acid had the compositions $Zr(OH)_{2.67}(C_2O_4)_{0.67}$ and $Zr(OH)_{2.4}(C_2O_4)_{0.8}$.

The complex formed on re-solution of the basic zirconium oxalate was not readily precipitated with alkalis : *e.g.*, the acid liberated by the interaction of 100 c.c. of *M*/100-zirconium tetrachloride and 100 c.c. of *N*/10-sodium oxalate was neutralised (phenolphthalein) by 35·3 c.c. of *N*/10-sodium hydroxide without a precipitate forming, and indeed only a slight opalescence was produced when sufficient alkali had been added to convert all the zirconium salt into the hydroxide and the solution boiled (40 c.c.).

The titration curve shows that a large concentration of hydrogen ions persisted throughout the whole reaction, p_H being 2·32 at 60 c.c., 3·10 at 80 c.c., and 3·64 at 100 c.c. There occurred a small inflexion just after 50 c.c. of sodium oxalate had been added, which indicated the stage at which oxalate ions had been added in an amount just sufficient to combine with the hydrogen ions from the first stage of dissociation to form HC_2O_4' ions (compare oxalic acid titration curve, *loc. cit.*). Thereafter the hydrogen-ion concentration arose from the ionic equilibrium $HC_2O_4' \rightleftharpoons H^{\cdot} + C_2O_4''$.

The zirconium hydroxide is present in the oxalate solution probably in the colloidal state, having been rendered so by combination with or adsorption of oxalate ions through the interplay of slight chemical forces. As the first stage of the ionisation of oxalic acid is that of a strong acid, there is reason to believe that this acid would, like hydrochloric or nitric acid, be capable of maintaining zirconium hydroxide in solution. Two molecules of oxalic acid, which on valency grounds should react with zirconium hydroxide to form the unknown zirconium oxalate, $Zr(C_2O_4)_2$, are only capable of reacting as if they were two molecules of a monobasic acid, thus :

$$Zr(OH)_4 + 2H{\cdot}HC_2O_4 \rightleftharpoons Zr(OH)_2(HC_2O_4)_2 + 2H_2O.$$

The basic zirconium hydro-oxalate, by analogy with the chloride (*q.v.*), would be strongly hydrolysed in solution, giving highly basic hydro-oxalate aggregates which would tend to remain in colloidal solution by virtue of the tendency which they may have to react with the hydrogen ions from the HC_2O_4' ions. The fact that sodium hydroxide does not readily precipitate zirconium hydroxide from oxalate solutions seems to show that zirconium ions are absent, or nearly so, from the solutions.

Sodium oxalate when added to a zirconium sulphate solution did not give a precipitate. An attempt was made to follow the changes in hydrion concentration during the addition of sodium oxalate by means of the hydrogen electrode, but the entry of a little potassium chloride, used in the junction liquid, into the zirconium sulphate

solution immediately rendered it precipitable. M/100-Zirconium sulphate (100 c.c.) was titrated and precipitation due to the potassium chloride began, but the precipitate did not redissolve until 85 c.c. of the oxalate solution had been added.

The clear solution obtained by adding sodium oxalate in not too great an excess to a zirconium sulphate solution gave a precipitate on addition of a little electrolyte, *e.g.*, the chloride or nitrate of sodium or potassium.

Chromium.—The curve in Fig. 2 is that of the titration of 100 c.c. of M/100-chrome alum with M/10-sodium oxalate. The solution was green initially, but became red towards the end of the titration. The diagram shows a very slight inflexion just after 30 c.c. of sodium oxalate had been added, *i.e.*, 3 mols. $Na_2C_2O_4$ to 1 mol. $Cr_2(SO_4)_3$, but the curve does not thereafter assume the upward course which it would take had simple double decomposition taken place. The very gradual diminution in hydrion concentration caused by the addition of sodium oxalate was due to the "buffering" action of the hydro-oxalate ions which had failed to react. The hydrogen-ion concentration at the end of the titration was $10^{-4\cdot4}$, which was greater than the precipitation value, $10^{-5\cdot3}$, for the hydroxide, but gradually approached it when larger quantities of sodium oxalate were employed. The solution to which 60 c.c. of M/10-sodium oxalate had been added was afterwards titrated with N/10-sodium hydroxide by means of the hydrogen electrode. Precipitation began when 1·85 equivalents had been added (p_H 5·4); thereafter the alkali caused only a partial precipitation and the graph of the change in p_H plotted against the amount of alkali added was rectilinear instead of curved, as is usually the case for precipitation by alkali. The slow change in hydrion concentration appears to have been caused by slight decomposition of the basic complex.

Some experiments were made to ascertain the conditions which rendered the solutions non-precipitable by alkalis. A mixture of M/10-chrome alum (1 mol.) and M/10-sodium oxalate (3 or 6 mols.) at room temperature gave a precipitate on treatment with N/10-sodium hydroxide; but if it had been first boiled and then cooled, no precipitate was obtained. Non-precipitable solutions were also produced by keeping. For example, two solutions, each 250 c.c., containing 30 and 60 c.c., respectively, of M/10-sodium oxalate and 10 c.c. of M/10-chrome alum, were kept over-night; the one containing the larger quantity of oxalate failed to give a precipitate with alkali.

An interesting gradation in colour was observed in a series of solutions, of the same concentration with respect to chrome alum but containing different quantities of sodium oxalate, the smallest

being 3 mols. (to 1 mol. of the sulphate), which had been boiled for the same length of time (a few minutes) and then kept over-night. They were all red in transmitted light, but had a green tinge in reflected light; the redness increased in intensity with increasing molar proportion of sodium oxalate. This may have been due to the effect of the diminishing hydrogen-ion concentration on the basic chromium oxalate complexes, produced by the increasing amounts of sodium oxalate. The solutions gave no precipitate in the cold on treatment with alkali, but a precipitate slowly formed on boiling. If the alkali was added in amounts just sufficient to convert the chromium salt into chromium hydroxide, precipitation took place after about a day. These alkaline solutions were also coagulated by the addition of 2 or 3 c.c. of saturated potassium chloride solution. Solutions which had been rendered non-precipitable by keeping only were very slightly more hydrolysed than the others.

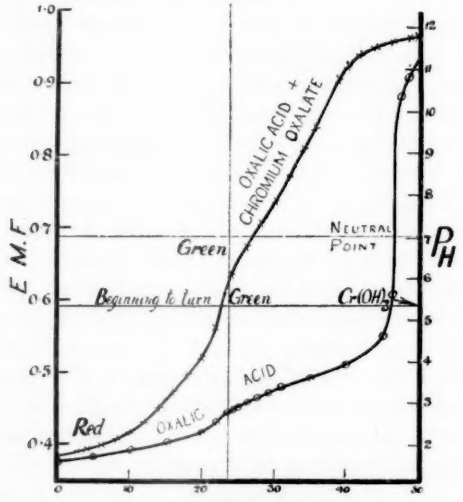
An oxalic acid solution of chromium hydroxide was prepared by boiling a chromic acid solution with oxalic acid until reduction was complete. The solution so obtained was claret-red and was not immediately precipitable by alkalis; on evaporation, it gave a green mass and oxalic acid crystals. From such a solution another was prepared which contained oxalic acid and chromium hydroxide in the proportions required by Werner's hypothetical tribasic chromi-oxalic acid, $H_3[Cr(C_2O_4)_3]$ (*Ber.*, 1912, **45**, 3061). The molar ratio may therefore be represented as $3H_2C_2O_4 : Cr_2(C_2O_4)_3$. The quantity of free and combined oxalic acid in 100 c.c. of the solution was equivalent to 51 c.c. of $N/10$-alkali, and on the latter method of representing the formula one-half of this, 25·5 c.c., may be regarded as combined with the chromium. This solution was titrated with 0·1082N-sodium hydroxide at 18° by means of the hydrogen electrode. The titration curve is given in Fig. 3. (The lower curve represents the titration, with the same alkali, of 51 c.c. of $N/10$-oxalic acid diluted to 100 c.c.) In reply to the objection that such a solution cannot possibly supply any information concerning Werner's hypothetical acid, it may be mentioned that the acid solution has the peculiar properties of Gregory's double salt,

$$3K_2C_2O_4,Cr_2(C_2O_4)_3,6H_2O,$$

which Werner regarded as a salt, $K_3[Cr(C_2O_4)_3]$, of his complex hypothetical acid and named potassium trioxalochromiate. The titration curve gives no evidence of the existence of a tribasic acid, but is composed of two distinct sections. Although no precipitate formed, it is significant that the claret-red solution began to turn green just when the hydrion concentration had become that at which chromium hydroxide is normally precipitated. This suggests that the colour is in some way related to the hydroxide itself.

The fact that the first half of the reaction terminated with an inflexion in the curve and a change in colour seems to be connected with the great difference between the two stages of ionisation of oxalic acid. The simplest explanation is to regard the chromium in the original solution as combined almost entirely with HC_2O_4 radicals, thus: $Cr(OH)_2 + 3H{\cdot}HC_2O_4 \longrightarrow Cr(HC_2O_4)_3 + 3H_2O$. The relatively large hydrion concentration could then be accounted for by slight hydrolysis having taken place owing to some little reaction with the hydrions from the hydro-oxalate ions. The first half of the titration would therefore be mainly that of the hydrogen ions from the large amount of HC_2O_4 ions with the added hydroxyl ions, and

FIG. 3.



therefore the range of hydrion concentration covered would be approximately that covered in the second half of the oxalic acid titration. The high initial concentrations in the chromium titration being excluded, it will be seen that the two ranges are comparable. When exactly half the theoretical amount of sodium hydroxide had been added, the reaction $3NaOH + Cr(HC_2O_4)_3 \rightleftharpoons 3H_2O + Cr(NaC_2O_4)_3$ may be considered to have taken place, and the second half of the sodium hydroxide would therefore have to react with the double sodium chromium oxalate to form a basic oxalate, probably associated with some sodium. The second portion of the chromium curve shows that only a part of the theoretical amount of the alkali had reacted, for the solution became alkaline on addition of considerably less sodium hydroxide than in the case of the oxalic acid

titration. Therefore, if x be the fraction of sodium hydroxide which had reacted, the reaction may be represented by the equation: $Cr(NaC_2O_4)_3 + 3xNaOH \rightleftharpoons Cr(OH)_{3x}(NaC_2O_4)_{3-3x} + 3xNa_2C_2O_4$.

The basic chromium oxalate complex is probably capable of ionising, but not so much so that it would produce in the solution the concentration of chromium ions requisite for precipitation. From the titrated solution to which 60 c.c. of 0·1082*N*-sodium hydroxide had been added, *i.e.*, 12·9 c.c. in excess of that required for the complete decomposition of the chromium oxalate, the chromium was completely precipitated after 24 hours, and, like the previous solutions, those which had been rendered just alkaline were also immediately coagulable on addition of a few c.c. of saturated potassium chloride solution and shaking. These observations seem to point to the colloidal nature of the basic oxalate complexes.

The absorption spectra of solutions representing different stages of the titration were examined. The solutions corresponding to the first half of the reaction absorbed light in the red, yellowish-green, and extreme blue regions. The absorption in the blue region was fairly uniform throughout the titration, whereas the absorption band in the green became considerably reduced in the second half. The chief change in absorption appeared suddenly in the red region almost immediately after the middle point of the titration had been passed; for the solution corresponding to the end of the titration, the band extended over the whole red field and partly into the orange. These absorptions were probably due to the size of the semi-colloidal particles. Lapraik's researches on the absorption spectra of chromium solutions (*J. pr. Chem.*, 1892, **47**, 305) included that of a colloidal solution of chromium hydroxide prepared by dialysing chromium chloride for some months, and also of chromium hydroxide suspended in water. He stated that the close resemblance between the absorption spectra of solutions of chromium hydroxide in several organic acids, including oxalic and some hydroxy-acids, despite the great difference in the molecular complexity of the acids used as solvents, suggested the probability of the absorption spectra being due mainly to the chromium hydroxide or oxide, and not to its compounds with the solvents. This constitutes strong support for the view that solutions of chromium salts of weak acids are essentially colloidal.

E. A. Werner (J., 1904, **85**, 1438) made the interesting observation that chromium hydroxide dissolves in hot oxalic acid solution to the extent required by the formula $Cr_2(C_2O_4)_3$. This, however, is no evidence for the existence of chromium oxalate in the solution, for solutions of the chromium salts of strong acids may be rendered basic beyond the point corresponding with the formula $Cr(OH)R_2$,

before any precipitation takes place. Hence in Werner's solution probably little more than the ions from the first stage of the dissociation of the oxalic acid combined with the chromium hydroxide, and this was present largely as a basic chromium hydro-oxalate; a small proportion of the second-stage hydrogen ions may have entered into reaction. Such an explanation would account for the anomalous conductivity data obtained by Rosenheim (*Z. anorg. Chem.*, 1896, **11**, 225) for a solution containing chromium oxide and oxalic acid in the proportion 1 : 3; he could obtain from the data no conclusive evidence that the substance in solution was either a free complex acid or a chromium salt of a complex chromioxalic acid.

The formula of the hypothetical tribasic chromioxalic acid is based on Rosenheim's measurements (*Z. anorg. Chem.*, 1896, **11**, 196, 225; 1899, **21**, 8) of the conductivity of solutions of double oxalates having the formula $3R_2C_2O_4,Cr_2(C_2O_4)_3,xH_2O$, where R is K, Na, or NH_4. Regarding these as complex salts, $R_3[Cr(C_2O_4)_3]$, he found that the difference between Λ_{1024} and Λ_{32} (where Λ is the conductivity of

$$1/3R_3[Cr(C_2O_4)_3])$$

varied from 32·4 to 35·8 for the three salts, and thence deduced the tribasicity of the complex acid, $H_3[Cr(C_2O_4)_3]$. It may be pointed out that there is no accord between Rosenheim's data for the potassium salt solutions and the earlier values of Kistiakovsky (*Z. physikal. Chem.*, 1890, **6**, 98). Rosenheim's figures also show that the ammonium salt is much more ionised than the potassium salt. The conductivities of the sodium and ammonium salts measured by Burrows and Walker (J., 1923, **123**, 2738) are somewhat lower than those of Rosenheim, but the differences Λ_{1024}—Λ_{32} are 29·3 and 32·9, respectively. By means of their cryoscopic and conductivity measurements these authors were able to show that in those solutions which were more dilute than 1/16-molar the number of ions into which each molecule of the salt dissociated was greater than 4. They concluded that it is only in comparatively concentrated solutions, greater than $M/10$, that the salt $R_3[Cr_2(C_2O_4)_3]$ dissociates into $3R^{\cdot}$ and $[Cr(C_2O_4)_3]'''$, and that at higher dilutions either the salt hydrolyses, giving ROH and $H_3[Cr(C_2O_4)_3]$, or the complex anion dissociates still further. The evidence for the existence of the complex tribasic chromioxalic acid is therefore inconclusive.

Some experiments have been carried out on Gregory's salt, $3K_2C_2O_4,Cr_2(C_2O_4)_3,6H_2O$ (*vide* Graham, "Chemical and Physical Researches," Edinburgh, 1876, p. 369). It was obtained in deep blue needles by allowing to crystallise a solution, containing chromic anhydride, potassium oxalate, and an excess of oxalic acid, which had been boiled until the anhydride was completely reduced

[Found : Cr, 10·7; C_2O_4, estimated by Burrows and Walker's method (*loc. cit.*), 54·1. Calc.: Cr, 10·7; C_2O_4, 54·2%].

On addition of *N*/10-sodium hydroxide to an *M*/120-solution of the salt there was no immediate reaction, as shown by hydrogen electrode measurements, but the red solution on becoming alkaline turned green, and when sufficient alkali had been added to convert the chromium oxalate into chromium hydroxide and the solution kept for 12 hours, it became opalescent and addition of a little potassium chloride caused precipitation. Addition of potassium chloride to a solution rendered just alkaline produced opalescence within a few minutes and the chromium was completely precipitated as the hydroxide in the course of 2 hours.

Werner made use of Gregory's salt in the development of his theory of "mirror-image isomerism." He suggested that the substance, regarded as the salt of a complex acid, should show a type of molecular asymmetry and be resolvable into optically active isomerides. The six molecules of water were regarded as water of crystallisation, and not of constitution as in the case of the hexahydrated chromium chloride. He achieved a fugitive resolution, by means of strychnine, in which water must have played an important part, for the optical activity disappeared much more quickly in aqueous than in acetone solutions. Jaeger (*Rec. trav. chim.*, 1919, **38**, 245) obtained much larger rotations. Rideal and Thomas (J., 1922, **121**, 196) found that the resolved salt on dissolution left a small, insoluble residue. This is surprising in view of the great ease with which the double oxalate dissolves. Their suggestion that the speedy loss in optical activity is due to decomposition of the complex anion into a less complex one seems to be confirmed by the *E.M.F.* measurements of Thomas and Fraser (J., 1923, **123**, 2973).

As water appeared to be the important factor in those optical rotation experiments, measurements have been made with the hydrogen electrode to ascertain if any parallel hydrolytic change occurs. The *P.D.* between a hydrogen electrode immersed in 100 c.c. of water at 18° and the normal calomel electrode, with saturated potassium chloride solution as junction liquid, was measured; 0·8123 g. of Gregory's salt was then rapidly dissolved in the water, and the *E.M.F.* observed every few minutes over a period of several hours. The results, which are in Table III, showed that

TABLE III.

Mins.	0	5	15	29	41	52
p_H	6·67 (water)	7·03	7·05	6·22	5·69	5·64
Mins.	70	93	105	138	180	20 hrs.
p_H	5·56	5·49	5·39	5·36	5·32	5·33

immediately following dissolution the hydrion concentration gradually increased until the p_H had become 5·49 (93 minutes); thereafter the change was much slower and the p_H became constant (5·33) after 12 hours and remained so during the next 20 hours. This p_H happens to be that at which chromium hydroxide is ordinarily precipitated. If the chromium oxalate in the salt were in a condition similar to that of the chromium salts of strong acids, a considerably higher hydrogen-ion concentration would have been produced. On referring to Fig. 3, it will be seen that the p_H (6·0) attained when the quantity of sodium hydroxide added was that required to form $3Na_2C_2O_4,Cr_2(C_2O_4)_3$ (indicated by the vertical line through the mid-point) was a little higher than the precipitation p_H of chromium hydroxide, probably owing to some decomposition of the oxalate complex having taken place. It therefore seems likely that the existence of the double salt may be due to the two different degrees of reactivity of oxalic acid, and that the change in hydrion concentration that occurs on its passing into solution may be due to the formation of basic complexes as suggested by the solution reaching the precipitation p_H of the hydroxide.

The concentration of oxalate ions in these complex salt solutions is small, for calcium chloride fails to give an immediate precipitate. Instead of being due to a complex anion, this may be equally well accounted for by the view now put forward, that the greater part of the oxalate ions is, in effect, removed from the solution in the form of colloidal complexes.

The fact that double oxalates of the general formula

$$3R_2C_2O_4,M_2(C_2O_4)_3$$

exist, where M may be tervalent iron, chromium, or aluminium, seems to be attributable to the nature of oxalic acid. The bases of these elements are so weak that it is exceedingly doubtful whether they are capable of entering into reaction to form normal oxalates, and yet in conjunction with the alkali metals they form well-defined compounds. There seems to be little doubt that the weak bases enter into combination with the HC_2O_4-ions, leaving the C_2O_4 ions to the alkali metals.

Aluminium.—The curve in Fig. 2 represents the hydrogen electrode titration of 100 c.c. of 0·005*M*-aluminium sulphate with 0·05*M*-sodium oxalate. No precipitate appeared, although the precipitation p_H of aluminium hydroxide was soon exceeded. The curve was only slightly inclined during the addition of the first 30 c.c. of sodium oxalate [*i.e.*, 3 mols. $Na_2C_2O_4$ to 1 mol. $Al_2(SO_4)_3$] and the corresponding p_H's differed but slightly from the precipitation p_H (4·14) of aluminium hydroxide, which was attained when 10 c.c. of sodium oxalate had been added. This suggests that aluminium

hydroxide, although it was not precipitated, existed in the solution in a more or less nascent state. Also the fact that the sodium oxalate in excess of 30 c.c. produced a gradual change in hydrion concentration, instead of an almost instantaneous fall to a concentration of the order produced by free sodium oxalate, shows that equilibria were being set up between the hydro-oxalate ions, which had failed to react with the aluminium hydroxide, and the oxalate ions from the added sodium oxalate. After the addition of 100 c.c. of $N/10$-sodium oxalate, the solution was titrated with $N/10$-sodium hydroxide; it became alkaline to phenolphthalein when 2·13 equivalents of sodium hydroxide (to one atom of aluminium) had been added, but no precipitate formed. Three equivalents of alkali, which were sufficient to convert all the aluminium salt into hydroxide, were then added; a precipitate appeared only after some time.

III. *Sodium Tartrate Titrations.*

Tartaric acid is comparatively weak in its first stage of ionisation, $K_1 = 1{\cdot}27 \times 10^{-3}$, and much weaker in its second stage, $K_2 = 9{\cdot}65 \times 10^{-5}$ at 18° (J., 1925, **127**, 1905). Of the metallic bases studied in these investigations, the only two that give basic tartrates on treatment with sodium tartrate are the very weak bases thoria and zirconia; these also dissolve in excess of the precipitant to give complex solutions which are not precipitable by alkalis. The reactions between zirconium, thorium, aluminium, beryllium, chromium, zinc, and lanthanum salts and $N/10$-sodium tartrate have been followed with the hydrogen and the normal calomel electrode. The titration curves of 100 c.c. of each of the solutions at 18° are in Fig. 4.

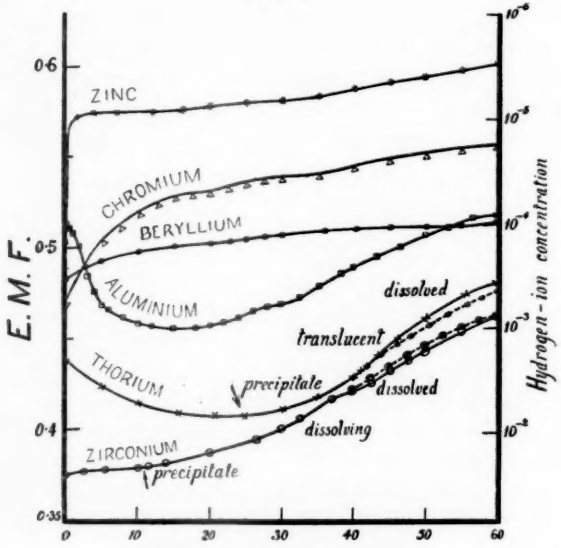
Zirconium.—The curve (Fig. 4) shows the changes in hydrion concentration that occurred during the addition of $N/10$-sodium tartrate to 100 c.c. of $M/100$-zirconium chloride. A gelatinous basic tartrate began to be precipitated when 10 c.c. of sodium tartrate had been added (p_H 1·66), but it began to redissolve on addition of 30 c.c. With 40 c.c., the solution was translucent, but became clear with 42·5 c.c.

The precipitate corresponding with the addition of 20 c.c. of $N/10$-sodium tartrate was produced by mixing large volumes of the reactants, the supernatant liquor being poured off, and the precipitate washed by decantation. It passed entirely into a translucent colloidal solution. The precipitate had therefore to be freed from the adhering liquor as completely as possible by pressing between filter-paper; some sodium tartrate, however, remained [Found in the air-dried precipitate: ZrO_2, 39·7; C (by "wet" combustion with chromic acid), 7·1%]. If the water content is neglected,

the composition of the precipitate may be expressed by the formula $ZrT_{0.45}(OH)_{3.1}$.*

In order to get some idea of the amount of titratable acid in these zirconium tartrate solutions, various quantities of $N/10$-sodium tartrate were added to 100 c.c. of $M/100$-zirconium chloride, and the resulting solutions titrated with $N/10$-sodium hydroxide. The results are in Table IV: a = c.c. of tartrate added, and b and c

FIG. 4.



= c.c. of $N/10$-alkali required to produce neutrality to phenolphthalein at 18° and 100°, respectively.

TABLE IV.

a	10	20	30	40	60	80
b	33·2	33·1	33·0	33·1	33·2	33·2
c	34·9	34·6	35·0	34·3	34·1	34·2

The alkali produced a precipitate, which did not redissolve, from the solution to which 10 c.c. of sodium tartrate had been added, but the precipitates that formed initially in the 20 c.c.- and 30 c.c.-solutions redissolved when 25 c.c and 14 c.c., respectively, of the alkali had been added. If no hydrolysis of the complex tartrate occurred, the table shows that, no matter how much sodium tartrate

* Throughout this paper T denotes $C_4H_4O_6$.

had been added, the quantity of free acid in the solution at 18° was equivalent to about 33·1 c.c. of N/10-sodium hydroxide, or 3·31 equivs. to 1 atom of zirconium. Under these conditions, the simplest formula for the basic complex in these solutions is $ZrT_{0.35}(OH)_{3.3}$, which is in fair agreement with that obtained for the imperfectly washed, basic precipitate, *viz.*, $ZrT_{0.45}(OH)_{3.1}$.

To confirm the existence of this complex in solution, and to show that the free acid was tartaric, the following titration was made. The change in hydrion concentration which occurred after 40 c.c. of N/10-sodium tartrate had been added was what would be expected to occur on addition of sodium tartrate to a solution containing free tartaric acid only. A solution (140 c.c.) was therefore prepared containing 33·1 c.c. of N/10-tartaric acid, which appears to be the amount of acid liberated on addition of the first 40 c.c. of sodium tartrate in the zirconium titration. The *E.M.F.* of the solution, measured with the hydrogen electrode against the normal calomel electrode, was 0·422 volt (the *E.M.F.* for the corresponding stage of the zirconium titration was 0·421 volt). Increasing quantities of N/10-sodium tartrate were now added; the voltages obtained are shown in the diagram by the broken line just above the zirconium curve. During the addition of the first 20 c.c. of N/10-sodium tartrate, *i.e.*, corresponding to 60 c.c. in the zirconium titration, the broken curve lay at a distance representing 3 millivolts at most from the zirconium curve, but during the addition of the next 40 c.c. (*i.e.*, corresponding with 60 to 100 c.c. in the zirconium titration) the two curves became coincident.

Tartaric acid also precipitates a basic tartrate from zirconium chloride solutions, but a considerably larger excess is required to effect its re-solution than in the case of sodium tartrate. For example, the precipitate formed when N/10-sodium tartrate was added to 100 c.c. of M/100-zirconium chloride solution required just over 40 c.c. for both precipitation and dissolution, whereas, when N/10-tartaric acid was used, re-solution did not occur until about 150 c.c had been added. The precipitate so formed dissolved readily in alkali, and the composition of the soluble complex thereby produced appeared to be the same as that in the sodium tartrate solutions. It may be that re-solution was actually due to the sodium tartrate which was formed, as may be seen from the following experiment. The heavy, gelatinous precipitate produced by adding N/10-sodium hydroxide to a mixture of 100 c.c. of M/100-zirconium chloride and 40 c.c. of N/10-tartaric acid dissolved when about 45 c.c. had been added, and the solution became alkaline to phenolphthalein with 73·2 c.c., which shows that the composition of the complex must have been $ZrT_{0.34}(OH)_{3.32}$.

The last column of Table IV shows that the complexes underwent very little decomposition in boiling alkaline solution.

The solubility of the basic zirconium tartrate precipitates in sodium hydrogen tartrate is less than that in the neutral tartrate, but greater than that in the free acid. The limiting amount of sodium tartrate to be added to a zirconium chloride solution to render it non-precipitable by alkali appears to be about 1 molecular proportion. With this proportion, a precipitate is obtained, but it dissolves on the addition of alkali; at a stage, however, before the solution becomes alkaline.

Thorium.—The curve (Fig. 4) represents the titration of 100 c.c. of $M/100$-thorium chloride with $N/10$-sodium tartrate. It is remarkable in that it shows that the addition of a normal tartrate rendered the solution more acid and then produced a precipitate. The p_H of the original solution was 2·68, but had fallen to 2·15 on addition of 25 c.c. of sodium tartrate, when precipitation began. By analogy with the formation of other basic precipitates—chromates, borates, and carbonates (Britton, this vol., p. 125)—it would have been expected that the precipitation of a basic tartrate would not have taken place until the precipitation p_H of the hydroxide had been attained, *viz.*, 3·5. A basic tartrate of thorium may also be precipitated by free tartaric acid; precipitation began at p_H 1·75 when 27·5 c.c. of 0·112N-tartaric acid were added to 100 c.c. of $M/100$-thorium tartrate, the large hydrion concentration being no doubt due to hydrochloric acid produced by hydrolysis.

The precipitates were flocculent and were not of definite composition. Haber's analyses (*Monatsh.*, 1897, **18**, 687) of precipitates obtained with tartaric acid, the water contents being disregarded, lay between those required for $ThT(OH)_2$ and $ThT_{1.33}(OH)_{1.33}$. The basic tartrate produced above from sodium tartrate and thorium chloride contained still less tartrate. The precipitate obtained on addition of 30 c.c. of sodium tartrate was, when air-dried, amorphous and contained 45·51% ThO_2 and 5·69% C (found by "wet" combustion), corresponding to the formula $ThO_2,0{\cdot}69T,11{\cdot}91H_2O$, or, the water content being disregarded, $ThT_{0.69}(OH)_{2.62}$.

Like basic zirconium tartrate, basic thorium tartrate redissolved when a little more than 40 c.c. of $N/10$-sodium tartrate had been added, *i.e.*, when the proportion was $2Na_2T : ThCl_4$. The acid liberated in the solution was equivalent to 26·2 c.c. of $N/10$-sodium hydroxide. Therefore, of the acid initially present as thorium chloride (= 40 c.c., expressed in terms of $N/10$-acid), 26·2 c.c. had been replaced by hydroxide and 13·8 c.c. by tartrate, and consequently the simplest formula of the basic thorium complex in the solution is

$$ThT_{0.69}(OH)_{2.62},$$

which happens to be also that of the precipitated basic tartrate. If it be assumed that 26·2 c.c. of $N/10$-tartaric acid were liberated during the interaction of 40 c.c. of $N/10$-sodium tartrate and 100 c.c. of $M/100$-thorium chloride, the concentration of the tartaric acid in the 140 c.c. of solution was $9{\cdot}33 \times 10^{-3}$, and K_1 of tartaric acid being taken as 1×10^{-3} (the effect of K_2 is negligible—see J., 1925, **127**, 1899), the p_H was 2·51. A solution (140 c.c.) of tartaric acid of this concentration was found, by means of the hydrogen electrode, to have exactly this p_H. The solution was titrated electrometrically with $N/10$-sodium tartrate; the titration curve, beginning at 40 c.c., is represented by the broken line lying a little below the thorium curve (Fig. 4). The differences in hydrogen-ion concentration shown in the two curves may be due to some interaction between the basic tartrate and the tartaric acid while the former is dissolving.

These solutions did not yield precipitates when treated with alkalis. Non-precipitable solutions could also be prepared by using less sodium tartrate. From the solutions employed in the titrations alkalis produced complete precipitation if 1 mol. or less of either tartaric acid or sodium tartrate had been added for each mol. of thorium chloride. Although $1\frac{1}{2}$ mols. of sodium tartrate produced a precipitate, this dissolved on addition of alkali and the solution became non-precipitable. Basic thorium tartrate, as was the case with the zirconium precipitate, required a considerable excess of tartaric acid to redissolve it, and the basic complex in the acid solution appeared to be the same as that in the sodium tartrate solution.

Rosenheim, Sammter, and Davidsohn (*Z. anorg. Chem.*, 1903, **35**, 424), in their investigation on complex thorium tartrates, isolated what they regarded as two series of salts containing the thorium in the anion, *viz.*, $R_2[ThOT_2]$ and $R_2[ThO_2T]$, where R = K, Na, or NH_4. Some of the products are described as "crusts." They attempted to ascertain which of these two salts existed in solution by determining the proportions of thorium nitrate, tartaric acid, and alkali which produced the maximum optical activity. These were stated to be $Th(NO_3)_4 : 2H_2T : 6ROH$, and therefore the authors concluded that the salt $R_2[ThOT_2]$ was indicated. On recalculation, however, these proportions are found to be in error, approximately 1 mol. of tartaric acid having been required instead of the 2 mols. stated, and the amount of alkali ranging from 5 to 7 mols. These are roughly the proportions required in the formation of 1 mol. of thorium hydroxide and 1 mol. of alkali-metal tartrate (compare the series $R_2[ThO_2T]$, *i.e.*, R_2T and ThO_2). The data of those authors show that such a solution was on the point of precipitation, for when the amount of thorium nitrate was increased in the ratio 8 : 7,

a precipitate appeared. As stated above, solutions of thorium chloride and sodium tartrate in equimolecular proportions fail to give a complex solution.

The amounts of $N/10$-sodium hydroxide required to neutralise the acid in these complex thorium tartrate solutions, when boiling, were a little greater than those required when the solutions were cold. Whatever the amount of $N/10$-sodium tartrate that had been added to 100 c.c. of $M/100$-thorium chloride, approximately 35 c.c. of $N/10$-sodium hydroxide were required to neutralise the boiling solution, which shows that the basic tartrate complex had slightly hydrolysed to $ThT_{0\cdot25}(OH)_{3\cdot5}$.

The fact that basic thorium tartrate cannot be redissolved by alkali except in the presence of sodium tartrate suggests that sodium tartrate or partly neutralised tartaric acid is responsible for its dissolution. It can scarcely be attributed to the formation of salts of a complex acid, and yet it seems to be due to some reaction taking place between the basic complex and the tartrate ions when present in sufficiently high concentration. A tartaric acid solution, on being gradually neutralised with alkali, therefore acquires a correspondingly increasing solvent capacity for both basic zirconium and basic thorium tartrates.

Aluminium.—The curve (Fig. 4) represents the titration of 100 c.c. of $M/200$-aluminium sulphate with $N/10$-sodium tartrate by means of the hydrogen electrode. Again, an unexpected increase in hydrion concentration was shown during the addition of the first 30 c.c. of tartrate solution (= 3 mols.). No precipitate separated and the solution remained clear. Hence, as the sodium tartrate was added, and sodium sulphate thereby formed, a considerable quantity of tartrate ions, instead of combining with the aluminium, was set free to form hydrotartrate ions, some free acid, and a basic aluminium tartrate complex in the solution. The maximum hydrion concentration, $10^{-3\cdot02}$, was attained when 15 c.c. of sodium tartrate solution had been added. This concentration was probably due mainly to hydrogen ions from the first-stage dissociation of the tartaric acid, the hydrotartrate ions having reacted with the aluminium hydroxide.

Titrations were made of the acid liberated in the solutions obtained by adding various quantities of $N/10$-sodium tartrate to 100 c.c. of $M/200$-aluminium sulphate. Ten c.c. of sodium tartrate were insufficient to produce a solution non-precipitable by alkali, but when 20 c.c. [*i.e.*, 2 mols. Na_2T for 1 mol. $Al_2(SO_4)_3$] or more were used, the solutions became non-precipitable and the amounts of alkali required to produce neutrality to phenolphthalein varied from 2·4 to 2·7 equivalents (for 1Al). In the boiling solutions, 2·8 equivalents

produced neutrality in each case. Therefore both in cold and in hot solutions a little tartrate remained firmly bound to the aluminium hydroxide. These experiments again seem to show that the non-precipitability is due to the existence of stable basic tartrates, the compositions of which, in the solutions studied, varied from $AlT_{0.3}(OH)_{2.4}$ to $AlT_{0.1}(OH)_{2.8}$.

Beryllium.—A small diminution in the hydrogen-ion concentration occurred in the titration of 100 c.c. of *M*/40-beryllium sulphate with *N*/10-sodium tartrate. This was not due to the formation of a less hydrolysed beryllium tartrate, for, as is shown by the curve (Fig. 4), no distinct change in hydrogen-ion concentration occurred when the requisite amount of sodium tartrate (50 c.c.) had been added. The small variation in the hydrion concentration was caused by equilibria set up between the added tartrate ions and the hydrotartrate ions, which, by failing to react with the beryllium, left it in the solution in the form of a basic tartrate. The high concentration of hydrotartrate ions was evidently due to their incapacity to react with that part of the beryllium hydroxide which gives rise to " soluble basic salts."

Solutions which contained one or more mols. of beryllium sulphate to one of sodium tartrate were completely precipitated by alkali, although solutions containing the reactants in the molar ratio 1 : 2 did not yield precipitates. The amounts of titratable acid in the complex tartrate solutions were approximately 1·53 equivalents for each molecule of beryllium sulphate taken, and consequently the composition of the final basic complex may be expressed by the formula $BeT_{0.24}(OH)_{1.53}$.

Rosenheim and Woge (*Z. anorg. Chem.*, 1897, **15**, 283) and Rosenheim and Itzig (*Ber.*, 1899, **32**, 3424) isolated two series of complex beryllium tartrates having the general formulæ $R_2[Be_4O_3T_2]$ and $R_2[Be_2OT_2]$, where R = K, Na, or NH_4. The individuality of these salts is questionable. Salts of the former series were obtained by evaporating hydrogen tartrate salt solutions, saturated with beryllium hydroxide, to syrups and allowing these to solidify, whereas salts of the latter series were prepared in the same way with the one exception that the calculated quantities of beryllium hydroxide were used. The salts were either glassy masses or microcrystalline crusts. Complex salts of the first type cannot give rise to non-precipitability, for, as Rosenheim and Woge state; ammonia produces a precipitate. As already mentioned, solutions containing beryllium sulphate and sodium tartrate in the molar ratio 2 : 1, which is that in $R_2[Be_4O_3T_2]$, are precipitable by alkalis. The latter workers have established, by means of the polarimetric method also used in the case of complex thorium tartrate solutions, that the important complex salt in the

solution was this particular compound, $Na_2[Be_4O_3T_2]$, from a study of solutions containing mixtures of beryllium sulphate, tartaric acid, and sodium hydroxide. The fact that the products which Rosenheim and Woge obtained by saturating solutions of acid salts with beryllium hydroxide should have corresponded to the formula $R_2[Be_4O_3T_2]$ is of interest in that the products may be considered as being made up of the neutral tartrate, R_2T, and the basic tartrate, $Be_4O_3T_2$, or $BeT_{0.25}(OH)_{1.5}$, which happens to be almost that suggested by these experiments to be present in the complex solutions.

Chromium.—The curve (Fig. 4) represents the hydrion concentration changes which occurred during the titration of 100 c.c. of $M/100$-chrome alum with $N/10$-sodium tartrate. The hydrion concentrations indicate that the amount of hydrotartrate ions liberated was less than that in the case of the corresponding beryllium titration. The difference appears to be accounted for by the fact that, although the precipitation p_H, 5·69, of beryllium hydroxide is a little higher than that of chromium hydroxide, 5·34, one-half of the beryllium hydroxide molecule is associated with the formation of soluble basic salts as compared with one-third in the case of chromium, and consequently a larger equivalent amount of acid is rendered available for reaction. The sodium tartrate caused the violet chromium salt solution to turn green.

The formation of complex chromium tartrate solutions which are not precipitable by alkali depends not so much on the amount of sodium tartrate added as on the treatment to which the solutions have been subjected, and in this respect appears to be similar to that of complex oxalate solutions. There is, however, the one difference that whereas oxalate solutions, on prolonged boiling with alkali, yield a precipitate, those of chromium tartrate in general do not. Chromium tartrate solutions, on boiling, become purplish-red, but if they are now treated with alkali at room temperature they turn green as soon as the precipitation p_H of the hydroxide is reached. As in the case of oxalate solutions, boiling caused the liberation of acid and the simultaneous formation of inert basic salt.

Zinc.—The curve (Fig. 4) is that of the titration of 100 c.c. of $M/50$-zinc sulphate with $N/10$-sodium tartrate. Although the sodium tartrate did not precipitate zinc hydroxide, the hydrion concentration on addition of the first 40 c.c. (when the molecular ratio was $Na_2T : ZnSO_4$) was reduced to nearly the precipitation p_H, 5·2, of zinc hydroxide. Titrations were made with sodium hydroxide and phenolphthalein of the acid liberated when varying quantities of $N/10$-sodium tartrate were added to 100 c.c. of $M/50$-zinc sulphate; the results are in Table V, where a = mols. of sodium tartrate per

mol. of zinc sulphate, and b and c = equivs. of sodium hydroxide required to produce a precipitate and neutrality, respectively.

TABLE V.

a	2	2·5	3	4	5
b	0·41	1·00	—	—	—
c	1·14	1·13	1·19	1·14	1·03

The table shows that the minimum quantity of sodium tartrate required to prevent precipitation by alkali was 3 mols. for 1 mol. of zinc sulphate (= 120 c.c.). This quantity is much greater than those required in the case of the weaker bases. Moreover, all the solutions referred to in the table gave a precipitate when boiled with alkali. The change in hydrion concentration after 40 c.c. of sodium tartrate solution had been added shows that not all the hydrions of the tartaric acid had reacted, and the amounts of alkali required to neutralise the acid which had failed to react indicate that the compositions of the basic tartrates in the complex solutions varied from $ZnT_{0\cdot49}(OH)_{1\cdot03}$ to $ZnT_{0\cdot41}(OH)_{1\cdot19}$.

Lanthanum.—When sodium tartrate was added to a lanthanum nitrate solution, a white, flocculent precipitate formed at p_H between 6 and 7 [Found in the air-dried precipitate: La_2O_3, 34·6; C (by "wet" combustion), 15·5. $La_2(C_4H_4O_6)_3,12H_2O$ requires La_2O_3, 34·75; C, 15·4%]. Czudnowicz (*J. pr. Chem.*, 1860, **79**, 39) and Holmberg (*Z. anorg. Chem.*, 1907, **53**, 87) prepared this salt, but based their formulæ on the lanthana content only, and reported that the water corresponded to $9H_2O$. Clève (*Bull. Soc. chim.*, 1874, **21**, 202) stated that the water content of the salt dried in a desiccator was $3H_2O$.

Lanthanum tartrate, although insoluble in water (Rimbach and Schubert, *Z. physikal. Chem.*, 1909, **67**, 192), is so readily soluble in mineral acids that when tartaric acid is added to a solution of a lanthanum salt of a strong acid no precipitate is formed; but one is obtained from a solution of lanthanum acetate. It is also readily soluble in alkalis and dissolves in an excess of sodium tartrate or tartaric acid solution. The following experiments were made to ascertain something of its nature in solution. Lanthanum tartrate was precipitated on addition of 30 c.c. of $N/10$-sodium tartrate to 30 c.c. of $N/10$-lanthanum nitrate. The solution became alkaline to thymol-blue on addition of 11·2 c.c. of $N/10$-sodium hydroxide, and the precipitate completely dissolved on addition of 13 c.c. The amount of alkali required for re-solution shows, if it be assumed that the alkali had been converted into sodium tartrate, that the lanthanum had passed back into solution as a basic tartrate,

$$LaT_{0\cdot85}(OH)_{1\cdot30}.$$

In another experiment, 50 c.c. of $N/10$-sodium tartrate were added to 30 c.c. of $N/10$-lanthanum nitrate, and the solution containing the suspended precipitate was titrated, by means of the hydrogen electrode, with $N/10$-sodium hydroxide. The precipitate dissolved at p_H 7·9, when 12 c.c. of alkali had been added, the soluble basic tartrate then being $LaT_{0.90}(OH)_{1.20}$, but the inflexion indicating the attainment of marked alkalinity did not occur until 14·4 c.c. had been added, and therefore the soluble basic lanthanum tartrate had become slightly decomposed to $LaT_{0.78}(OH)_{1.44}$. The curve obtained on adding more alkali showed that the basic tartrate was undergoing further decomposition. The following experiment gives some idea of the extent of the decomposition which takes place in alkaline solutions. Lanthanum tartrate (0·1960 g.) was shaken mechanically with 100 c.c. of 0·014N-sodium hydroxide for 24 hours; all the tartrate had then dissolved. The solution was titrated by means of the hydrogen electrode with $N/10$-hydrochloric acid, and the excess of free alkali was equivalent to 6·35 c.c. of the acid. The lanthanum tartrate therefore existed in the alkaline solution as $LaT_{0.59}(OH)_{1.82}$, and was much more basic than those mentioned above. In this titration, the basic lanthanum tartrate began to be precipitated when the free alkali had just been neutralised, and the p_H then attained was that required for the precipitation of lanthanum hydroxide.

Discussion.

The foregoing investigations show that complex tartrate solutions are essentially basic in nature. This is especially evident in the cases of the complex zirconium and thorium tartrate solutions produced by the re-solution, probably without change in composition, of the basic tartrates first precipitated. Unlike the complex solutions which were sometimes formed with acetates and oxalates, those of the tartrates are extremely stable. The basic tartrates, like the basic aggregates in solution, are strongly resistant to alkalis, which probably explains their non-precipitability by such means.

The existence of these basic tartrate complexes would also account for the properties of Fehling's solution. The fact that the ease of reduction to cuprous oxide is comparable with that of freshly precipitated cupric hydroxide suggests that the condition of the cupric salt in alkaline tartrate solutions is in some way related to that of cupric hydroxide itself, as would obtain in basic tartrate complexes.

The condition of copper tartrate on passing into these complex alkaline tartrate solutions is, at any rate, basic. For example, Kahlenberg (*Z. physikal. Chem.*, 1895, **17**, 586), Masson and Steele (J., 1899, **75**, 725), and Pickering (J., 1911, **99**, 169) found that the quantity of sodium or potassium hydroxide necessary to produce

alkalinity in a solution of copper tartrate varied from 1·25 to 1·36 mols., and therefore the basic complexes in the solutions must have varied from $CuT_{0.38}(OH)_{1.25}$ to $CuT_{0.32}(OH)_{1.36}$.

Previous workers attempted to account for the anomalies of complex tartrate solutions by regarding the heavy metal as being present in a complex anion. Masson and Steele obtained a substance, $K_3Cu_4C_{12}H_7O_{18},5H_2O$, by precipitation with alcohol from a copper tartrate solution which had been neutralised with 1·25 equivalents of potassium hydroxide. The substance, which was isolated as a dark blue, gummy mass (and therefore was of questionable character), was in effect composed of $3K_2T$ and $8CuT_{0.375}(OH)_{1.25}$ and was probably a mixture of potassium tartrate with a preponderance of basic copper tartrate. Their migration experiments on solutions of this substance are important in that they show that some copper had passed into the portion carrying the negative charge, but this may have been due equally well to the colloidal nature of the basic copper tartrate as to the presence of a complex copper anion. Pickering also obtained flocculent precipitates from copper tartrate solutions by adding alcohol. The unwashed precipitates (whose constitutions he tried to establish by regarding some of the copper as quadrivalent) contained variable quantities of potassium salt, all of which, together with some copper, could be removed by washing. Wark (J., 1923, **123**, 1815, 1826; 1924, **125**, 2004) has suggested that the complexity of solutions containing copper and malic acid is due to the formation of cuprimalic acid, $HCuC_4H_3O_5$, isomeric with the normal cupric malate.

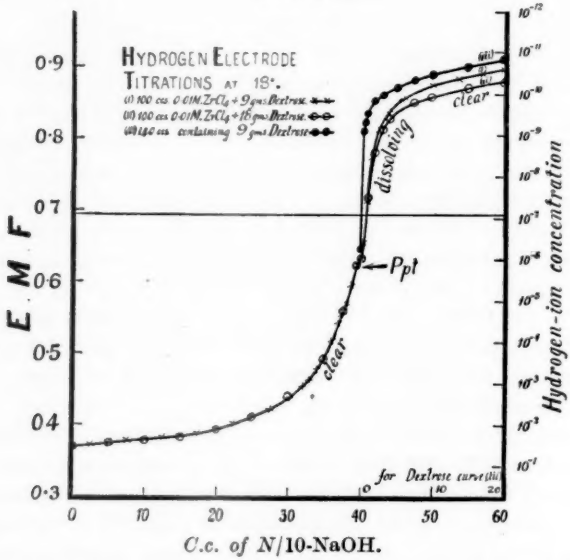
The formation of the complex tartrate solutions of zirconium and thorium by the re-solution of the basic precipitates seems to have been due to the sodium tartrate which was present, although it has not been possible to associate any precise quantity of the latter with that of the respective basic tartrates. Many attempts have been made to account for the complexity of tartrate solutions by assuming that their formation involves reactions with the hydrogen atoms of the hydroxy-groups. It is difficult, however, to imagine that zirconium hydroxide, for example, one of the weakest bases, should be capable of so reacting, when strong bases show so very little aptitude. If the hydroxy-groups of tartaric acid are weakly acidic (their acidity is so small that it is not measurable by any physical method), they might be able to react with metallic bases, provided that the products formed were insoluble and therefore were removed from the sphere of action. Such a condition would probably be satisfied if the bases which had combined passed into the dispersed particles of a colloidal solution.

Many hydroxy-compounds, such as the sugars and glycerol, have

a definite, though very slight, acid character (compare Michaelis and Rona, *Biochem. Z.*, 1913, **49**, 248) and their dissociation constants can be measured. The dissociation constant of glycerol as a monobasic acid at 17·5° is 7×10^{-15}, and, in fact, the presence of glycerol in an alkali solution has a barely measurable effect on the p_H. Yet its effect on a zirconium chloride or ferric chloride solution may be such that alkalis fail to precipitate the hydroxide.

The reaction which must take place between the glycerol and the metallic base provides an explanation of the well-known protective action on ferric oxide hydrosols prepared by dialysis of ferric

FIG. 5.



chloride–glycerol solutions. It is significant, too, that the hydrosols so prepared are clear in transmitted light. The glycerol may retard the growth of the colloidal particles.

If the behaviour of the hydroxy-groups of tartaric and other hydroxy-acids is due to their feebly acid character, then it seems that complex tartrate solutions are essentially protected colloidal solutions. The following electrometric titrations were carried out to test this view. Michaelis and Rona (*loc. cit.*) having shown that dextrose is a stronger acid ($K = 6{\cdot}6 \times 10^{-13}$; compare Britton, J., 1925, **127**, 1902) than glycerol, it was decided to use the former in the titrations. A solution (100 c.c.), $M/100$ with respect to zirconium chloride and $M/2$ with respect to dextrose (9 g. in 100 c.c.), was titrated with $N/10$-sodium hydroxide at 18° by means of the

hydrogen and the normal calomel electrode. The curve is shown in Fig. 5, the points obtained being marked by crosses. A very slight opalescence was produced by 38·5 c.c. of the alkali ($p_H = 5·22$), and a precipitate by 39·5 c.c. ($p_H = 5·89$). This began to dissolve when 40 c.c. (*i.e.*, $4NaOH : ZrCl_4$) had been added, and the solution was cleared by 50 c.c. In the titration of zirconium chloride solution alone (J., 1925, **127**, 2125), the solution first became visibly colloidal with 1·5 equivalents of alkali ($p_H = 1·86$), but in the present titration the effect of the dextrose was manifested in the delay of precipitation until nearly the whole of the alkali required to convert the zirconium chloride into the hydroxide had been added and the hydrogen-ion concentration had become extremely small, *viz.*, 10^{-6}. The fact that the solution remained clear until 3·85 equivalents of alkali had been added suggests that, although the dextrose was incapable of influencing the hydrogen-ion concentration of the solution, it had the effect of repressing the growth of the basic particles below the limit necessary to produce visible colloidality. Table VI, compiled from the observed voltages, shows that during the addition of the first 40 c.c. of alkali the zirconium chloride was more basic than $ZrCl(OH)_3$. The ionisation of dextrose is much too small to affect the hydrogen-ion concentrations of solutions whose p_H is less than 6, and consequently the hydrion concentrations of the basic zirconium chloride solutions have been regarded as coming entirely from the hydrolysed acid.

TABLE VI.

C.c. of *N*/10-NaOH.	*E.M.F.*	% Hydrolysis of un-neutralised part.	Atoms of Cl in $ZrCl_4$ neutralised.	Composition of basic zirconium chloride. Atoms per 1Zr. Cl.	OH.	Mols. of free HCl referred to 1Zr.
0·0	0·370	77·8	0	0·89	3·11	3·11
5·0	0·374	79·5	0·5	0·78	3·22	2·72
10·0	0·379	79·8	1·0	0·61	3·39	2·39
15·0	0·386	75·7	1·5	0·61	3·39	1·89
20·0	0·395	68·7	2·0	0·63	3·37	1·37
25·0	0·413	46·5	2·5	0·80	3·20	0·70
30·0	0·438	26·8	3·0	0·73	3·27	0·27
35·0	0·491	6·7	3·5	0·47	3·53	0·03
37·5	0·552	1·2	3·75	0·25	3·75	0·003
38·0	0·566	1·1	3·8	0·20	3·80	0·002
39·0	0·598	0·5	3·9	0·10	3·90	0·0005
39·5	0·623	0·4	3·95	0·05	3·95	0·0002
40·0	0·634	0	4	0	4	0

The last column shows that when the solution began to opalesce, with 38·5 c.c. of alkali, the amount of free acid had become negligible. It is remarkable that the dextrose was able to maintain the highly basic zirconium chloride (columns 5 and 6) in a solution which was quite clear. Borax and sodium carbonate also delay precipitation

by alkali until somewhat more than 3 equivalents have been added (this vol., p. 125).

In order to ascertain whether the dextrose had entered into any reaction which might have influenced the p_H of the solution during the re-solution of the zirconium hydroxide in the sodium hydroxide, a solution of 140 c.c. (*i.e.*, the volume of the titrated solution when the stoicheiometrical amount of alkali had been added) containing 9 g. of dextrose was titrated with $N/10$-sodium hydroxide. The data and dissociation constant figures of dextrose as a monobasic acid are given in a previous paper (J., 1925, **127**, 1902). In Fig. 5 the titration curve is the one beginning at 40 c.c. of $N/10$-sodium hydroxide given at the top of the diagram. By comparing the two curves, it will be seen that the presence of the zirconium hydroxide in the one solution caused a perceptible diminution in p_H, and consequently the hydroxide on dissolution must have combined in some way with the dextrose. It is difficult to understand how the zirconium hydroxide effected this increase in hydrogen-ion concentration. Had it reacted simply with the dextrose to form inert colloidal aggregates, this, in effect, would have been equivalent to the removal of some dextrose from the solution and therefore would have given rise to a diminished hydrion concentration. An increased hydrogen-ion concentration seems to be possible only by assuming that the zirconium hydroxide had, in combining with the dextrose, given rise to a complex acid slightly stronger than dextrose itself. All that the titration can be said to show is that dextrose does enter into some kind of reaction with the zirconium hydroxide in effecting its dissolution in alkali solutions.

A second titration was that of 100 c.c. of $M/100$-zirconium chloride and $M/1$-dextrose solution (18 g. in 100 c.c.). The increased amount of dextrose was without further effect during the addition of the first 40 c.c. of alkali, but tended to cause a more rapid re-solution of the zirconium hydroxide as the excess of alkali was added. The data for this curve are indicated by circles in Fig. 5.

Summary.

(1) Sodium acetate at the ordinary temperature fails to precipitate weak bases, although the precipitation p_H's of the respective hydroxides may be exceeded. An exception is the reaction with thorium sulphate solution. There is good evidence that weak metallic bases exist in complex acetate solutions as basic acetates.

(2) Sodium oxalate produces a basic precipitate from zirconium chloride solution through the incapacity of the hydrions from the second stage of dissociation of oxalic acid to react with zirconium hydroxide, but the precipitate dissolves in excess of the reagent.

The oxalate does not produce precipitates from solutions of salts of slightly stronger bases, *e.g.*, aluminium and chromium hydroxides, even although it is probable that very little reaction can take place between them and the hydro-oxalate ions. Observations on solutions of chromium hydroxide in oxalic acid and of potassium chromium oxalate suggest that both their properties and the existence of the series $3R_2C_2O_4,Cr_2(C_2O_4)_3$ arise from the nature of the reactants.

(3) The reaction of sodium tartrate with salts of thorium and aluminium in solution is remarkable in that increased hydrion concentrations are at first produced; in the case of thorium, a basic tartrate precipitate is formed, even although the hydrion concentration is considerably higher than that necessary for the precipitation of the hydroxide.

(4) Hydrogen electrode titrations of zirconium chloride solutions containing dextrose with sodium hydroxide show that some reaction must take place between the zirconia and the hydroxy-groups of dextrose.

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XXXIX.—*The Absorption of Gases by Colloidal Solutions.*

By ALOIS GATTERER.

ONE of the most important studies of colloid chemistry is that dealing with adsorption and absorption in colloidal solutions, for not only is it of considerable practical value, but also it may throw light on the structure of the colloids themselves. The study of gaseous absorption in particular may be expected to yield definite and valuable results because of the chemical and electrical neutrality of solvent and solute. Of the few investigations of this kind that have hitherto been made, those of Geffcken (*Z. physikal. Chem.*, 1904, **49**, 297) and Findlay and his co-workers (J., 1910, **97**, 536; 1912, **101**, 1459; 1913, **103**, 636; 1914, **105**, 291) are limited in their scope, being confined to comparatively few gases and solutions, to low concentrations and, above all, to one temperature, *viz.*, 25°.

Consequently, our knowledge of the absorptive power of colloidal

solutions is meagre and does not furnish a sufficiently broad experimental foundation for a trustworthy theory. A wide investigation of absorption has therefore been undertaken, with various colloidal solutions and at temperatures ranging from 5° to 25°. The colloidal solutions have been characterised by determinations not only of density and concentration but also of electrical conductivity, viscosity, the Tyndall effect, and absorption of light, for only in this way is it possible to define these complex systems so precisely that they can be exactly reproduced.

The observations here recorded refer only to two gases, carbon dioxide and acetylene, and to two colloidal solutions, ferriferrocyanide and ferric hydroxide; the former were chosen because of their acidic and neutral character respectively, and the latter because they are, respectively, positive and negative colloids.

Experimental.

Preparation of Solutions.—Ferriferrocyanide. The solution was prepared according to Zsigmondy (" Kolloid Chemie," 1920, 3rd ed., p. 300) by mixing $2N$-solutions of sodium ferrocyanide and ferric chloride. The precipitate was carefully washed, redissolved in a small quantity of the ferrocyanide, and the solution was concentrated by heating in a vacuum. The maximum concentration obtained was about 8%.

Ferric hydroxide. A solution of pure ferric hydroxide in acetic acid was diluted and, after the method of Péan de St. Gilles, boiled until the ratio of acetic acid to ferric hydroxide became 1 : 30—1 : 60. The solution was then evaporated, not under atmospheric pressure, but under reduced pressure, whereby a much higher degree of dispersion, as shown by the Tyndall effect (compare Figs. 1 and 2), was obtained. This more highly dispersed solution appears to be intermediate between the solution of Graham and that of P. de St. Gilles.

Preparation of Gases.—The carbon dioxide was carefully washed and its purity was confirmed by the value obtained for its solubility in distilled water. Acetylene was generated from calcium carbide and freed from impurities by treatment with chromic acid and potassium hydroxide and by absorption in acetone. Analyses of the purified product by means of ammoniacal cuprous chloride showed residues of 0, 2, and 3 c.c. in 100 c.c.

Apparatus and Outline of Method.—The method of Ostwald was employed to measure absorption (Ostwald-Luther, " Handbuch der Physicochemischen Messungen," 1910, 3rd ed., p. 246). The solutions were freed from air by boiling in a vacuum and, without contact with air, transferred to the vacuum mixing vessel at 25°.

The gases were saturated with water vapour at the same temperature. Five measurements were made with a given solution at five different temperatures, the process being repeated after an interval of several hours to check the former results. The calculation of the solubility is based on the formula (see Ostwald-Luther, *op. cit.*)

$$l = \left[V_{b_1} \frac{T_a(b_1 - h_{b_1})}{T_{b_1}(b_1 - h_a)} - V_{b_2} \frac{T_a(b_2 - h_{b_2})}{T_{b_2}(b_2 - h_a)} - V_a \right] \frac{1}{V_\beta},$$

where l = Ostwald's solubility; V_{b_1} = initial volume of gas in the burette at temperature T (abs.) and pressure b_1; V_{b_2} = final volume of gas in the burette; T_a = absolute temperature of the thermostat; T_{b_1} and T_{b_2} = initial and final temperature, respectively, of gas in burette; b_1 and b_2 = pressure of the atmosphere at commencement and end of experiment; h_a, h_{b_2}, and h_{b_1} = tension of water vapour at T_a, T_{b_2}, and T_{b_1}, respectively; V_a = volume of liquid withdrawn, measured at T_a; $V_\beta = V - V_a$ = volume of liquid contained in the absorption vessel; and V = volume of the absorption vessel at temperature T_a.

The changes in volume of the solutions and of the mixing vessel at various temperatures were taken into consideration. The probable error was $\pm 0{\cdot}4\%$. In certain cases, owing to an exceedingly slow rate of absorption, the completion of this was not reached, and this may be the explanation of the lack of smoothness in some of the curves. The values of l are given either in percentages, *i.e.*, number of grams in 100 c.c. of solution, or in gram-equivalents. All values of volume are calculated for 20°. Although it is uncertain whether the colloids in question have definite chemical formulæ, yet for the sake of clearness the gram-equivalent of Prussian blue was taken as $1/12\ Fe_4[Fe(CN)_6]_3 = 71{\cdot}603$, and that of ferric hydroxide as $1/3\ Fe(OH)_3 = 35{\cdot}621$.*

Solubility of Carbon Dioxide in Solutions of Prussian Blue.

The values in Table I have been obtained by different workers for the solubility of carbon dioxide in water.

Findlay (*loc. cit.*) gives a somewhat lower value, *viz.*, 0·817 at 25°.

The solubility values (l) of carbon dioxide in solutions of Prussian blue are in Table II and Fig. 3 (unbroken lines).

* According to Hofmann ("Lehrbuch der Anorganischen Experimentalchemie," 1918, p. 641) soluble Prussian blue has the formula $Fe(CN)_6NaFe$. This, of course, would change the above equivalent weight. Hofmann's formula, however, is not generally accepted, and, moreover, does not agree with the author's results. Further, if Hofmann's formula is assumed, the results obtained by the gravimetric and the volumetric methods do not agree.

TABLE I.

	Bohr and Bock.*	Geffcken.†	Gatterer.‡			
			l.			
T.	*l.*	*l.*				Mean.
25°	0·829	0·8255	0·826	0·823	0·830	0·826
20	0·942	—	0·933	0·936	0·940	0·936
15	1·072	1·070	1·066	1·072	1·073	1·070
10	1·238	—	1·233	1·244	1·242	1·240
5	1·449	—	1·440	1·453	1·445	1·446

* *Wied. Ann.*, 1891, **44**, 318. † *Loc. cit.* ‡ In this and the following tables the exact temperatures are: 25·00°, 19·98°, 14·96°, 9·95°, and 4·97° instead of 25°, 20°, 15°, 10°, and 5°, respectively. In the solubility diagrams, the mean values in the tables are represented. For economy in space, the curves of different temperature intervals are moved closer together.

TABLE II.

	25°.	20°.	15°.	10°.	5°.
Soln. 1.	0·8424	0·9510	1·086	1·254	1·451
$c = 0·896N$	0·8418	0·9515	1·087	1·255	1·454
	0·8421	*0·9512*	*1·087*	*1·255*	*1·453*
Soln. 2.	0·8516	0·9617	1·095	1·262	1·463
$c = 0·51N$	0·8494	0·9610	1·092	1·265	1·466
	0·8505	*0·9613*	*1·093*	*1·264*	*1·464*
Soln. 3.	0·8566	0·9696	1·105	1·276	1·477
$c = 0·37N$	0·8588	0·9672	1·106	1·279	1·479
	0·8577	*0·9684*	*1·106*	*1·277*	*1·478*
Soln. 5.	0·8544	0·9653	1·100	1·270	1·472
$c = 0·178N$	0·8517	0·9613	1·096	1·267	1·472
	0·8530	*0·9633*	*1·098*	*1·268*	*1·472*
Soln. 4.	0·8430	0·9510	1·0850	1·254	1·463
$c = 0·126N$	0·8456	0·9568	1·092	1·263	1·469
	0·8443	*0·9549*	*1·089*	*1·258*	*1·465*

Mean values are printed in italics in all the tables.

The temperature coefficients of absorption of carbon dioxide in solutions of Prussian blue ($\Delta l/\Delta t$) are in Table III, and have been calculated from the results in Table II.

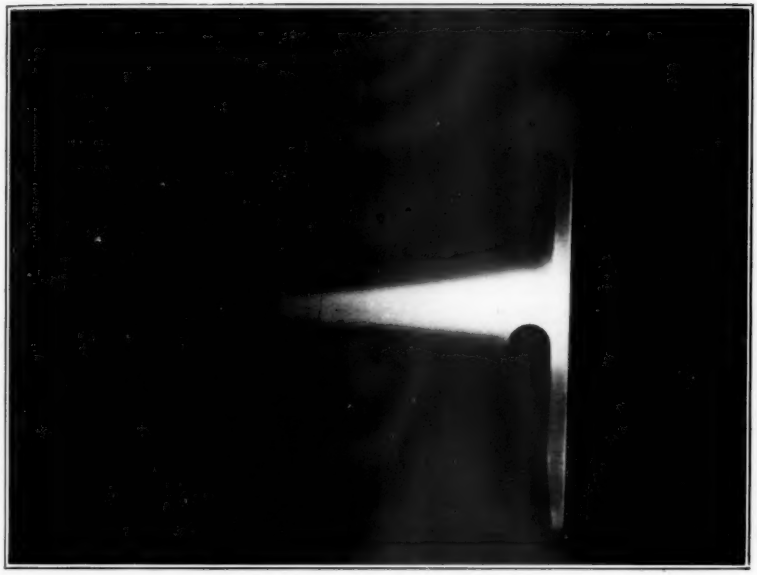
TABLE III.

Soln.	25—20°.	20—15°.	15—10°.	10—5°.
1	0·0218	0·0271	0·0336	0·0396
2	0·0221	0·0264	0·0342	0·0400
3	0·0221	0·0274	0·0342	0·0402
5	0·0221	0·0268	0·0340	0·0408
4	0·0219	0·0268	0·0338	0·0414
H_2O	0·0220	0·0268	0·0340	0·0412

Solubility of Carbon Dioxide in Solutions of Ferric Hydroxide.

In Table IV and Fig. 3 (broken lines) are the solubilities of carbon dioxide in solutions of ferric hydroxide at temperatures ranging from 5° to 25° in intervals of 5°, whilst in Table V are the temperature coefficients ($\Delta l/\Delta t$).

FIG. 1.



Tyndall effect for solution evaporated under atmospheric pressure.

FIG. 2.

Tyndall effect for solution evaporated in a vacuum.

[*To face p.* 302.]

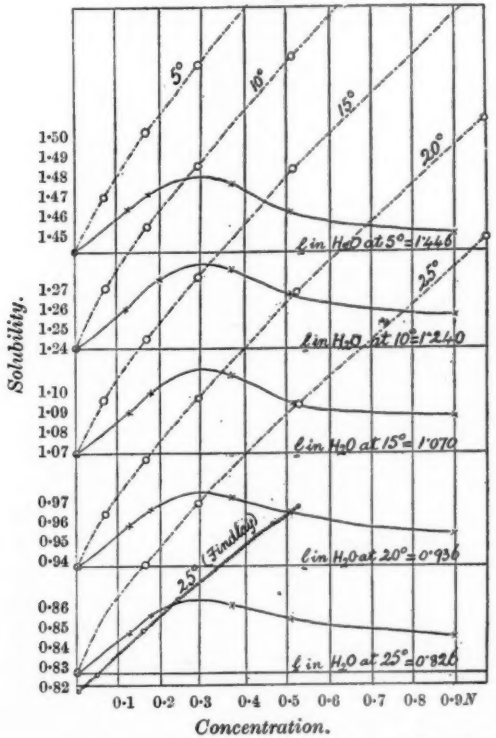
TABLE IV.

	25°.	20°.	15°.	10°.	5°.
Soln. 2.	0·8518	0·9601	1·093	1·264	1·467
$c = 0·071N$	0·8547	0·9619	1·098	1·271	1·476
	0·8533	*0·9610*	*1·095*	*1·267*	*1·471*
Soln. 1.	0·8788	0·9906	1·127	1·300	1·509
$c = 0·144N$	0·8740	0·9834	1·119	1·297	1·498
	0·8764	*0·9870*	*1·123*	*1·297*	*1·503*
Soln. 4.	0·9073	1·017	1·155	1·326	1·536
$c = 0·293N$	0·9053	1·016	1·153	1·326	1·533
	0·9063	*1·016*	*1·154*	*1·326*	*1·534*
Soln. 3.	0·9531	1·067	1·203	1·379	1·583
$c = 0·513N$*	0·9521	1·066	1·205	1·380	1·585
	0·9526	*1·066*	*1·204*	*1·379*	*1·584*
Soln. 5.	1·030	1·146	1·287	1·467	—
$c = 0·967N$	1·035	1·152	1·295	1·473	1·684
	1·032	*1·149*	*1·291*	*1·470*	*1·680*

* This value was obtained from a density determination.

FIG. 3.

Solubility of carbon dioxide in solutions of Prussian blue and ferric hydroxide.



—·—·— CO_2 in $Fe(OH)_3$. ——— CO_2 in $Fe_4[Fe(CN)_6]_3$.

TABLE V.

Soln.	25—20°.	20—15°.	15—10°.	10—5°.
2	0·0215	0·0268	0·0344	0·0408
1	0·0221	0·0272	0·0348	0·0412
4	0·0220	0·0276	0·0344	0·0416
3	0·0227	0·0276	0·0350	0·0410
5	0·0234	0·0284	0·0358	0·0420
H_2O	0·0220	0·0268	0·0340	0·0412

Solubility of Acetylene in Solutions of Prussian Blue.

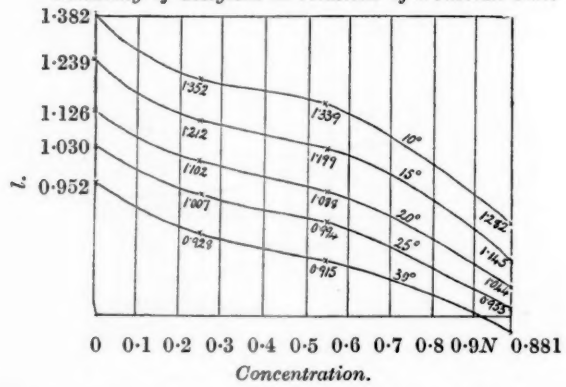
The following solubility values of purified acetylene in distilled water were obtained (Table VI).

TABLE VI.

T.	*l.*			Mean.
30°	0·951	0·950	0·954	0·952
25	1·030	1·028	1·031	1·030
20	1·126	1·125	1·127	1·126
15	1·239	1·239	1·241	1·239
10	1·381	1·383	1·383	1·382

FIG. 4.

Solubility of acetylene in solutions of Prussian blue.



The values of Winkler, according to unpublished communications (Landolt–Börnstein–Roth, "Physikalisch-Chemie Tabellen," 1912, p. 600), are calculated only to the second decimal place and, on the average, are smaller by 1·5—2% than those of the author, as the following figures show :—

	30°.	25°.	20°.	15°.	10°.
Abs. coeff. (Winkler)	0·84	0·93	1·03	1·15	1·31
Abs. coeff. from Table VI, mean values	0·858	0·944	1·049	1·175	1·330
Diff. %	2·1	1·5	1·8	2·1	1·5

Only a more accurate study of Winkler's experiments could determine whether or not this difference is due to impurities in the gas.

Table VII and Fig. 4 show the solubility of acetylene in solutions of Prussian blue, and Table VIII the temperature-coefficients per degree.

TABLE VII.

	30°.	25°.	20°.	15°.	10°.
Soln. II.	0·9286	1·007	1·100	1·210	1·351
$c = 0·250N$	0·9292	1·007	1·103	1·214	1·365
	0·9289	*1·007*	*1·102*	*1·212*	*1·358*
Soln. I.	0·9186	0·9966	1·089	1·199	1·335
$c = 0·548N$	0·9113	0·9908	1·086	1·199	1·343
	0·9149	*0·9937*	*1·088*	*1·199*	*1·339*
Soln. III.	0·8808	0·9543	1·042	1·147	1·276
$c = 1·028N$	0·8825	0·9512	1·046	1·142	1·289
	0·8816	*0·9527*	*1·044*	*1·145*	*1·282*
Soln. IV.					
$c = 0·75N$*	0·901	0·976	1·071	1·179	1·317

* This value was obtained from a density determination, and the corresponding values of l from the graph (Fig. 4).

FIG. 5.

Solubility of acetylene in solutions of ferric hydroxide.

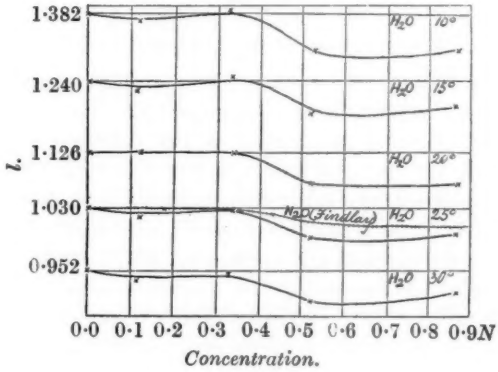


TABLE VIII.

Soln.	30—25°.	25—20°.	20—15°.	15—10°.
II	0·0156	0·0190	0·0220	0·0282
I	0·0158	0·0188	0·0222	0·0280
IV	0·0150	0·0190	0·0216	0·0276
III	0·0142	0·0182	0·0202	0·0274
H_2O	0·0156	0·0192	0·0226	0·0286

Solubility of Acetylene in Solutions of Ferric Hydroxide.

The data are in Table IX and are shown by the curves in Fig. 5: the temperature coefficients are in Table X.

TABLE IX.

	30°.	25°.	20°.	15°.	10°.
Soln. III.	0·9405	1·020	1·109	1·229	1·372
$c = 0·871N$	0·9394	1·016	1·112	1·225	1·366
	0·9400	*1·018*	*1·111*	*1·227*	*1·364*
Soln. II.	0·9360	1·015	1·111	1·226	1·368
$c = 0·521N$	0·9360	1·016	1·111	1·223	1·361
	0·9360	*1·016*	*1·111*	*1·224*	*1·364*
Soln. I.	0·9499	1·030	1·126	1·240	1·381
$c = 0·336N$	0·9492	1·028	1·126	1·243	1·386
	0·9495	*1·029*	*1·126*	*1·241*	*1·383*
Soln. IV.	0·9446	1·025	1·125	1·230	1·380
$c = 0·12N$	0·9426	1·024	1·129	1·233	1·378
	0·9479	1·027	1·123	1·236	1·378
	0·9450	*1·026*	*1·126*	1·236*	*1·379*

* More probable value.

TABLE X.

Soln.	30—25°.	25—20°.	20—15°.	15—10°.
III	0·0156	0·0186	0·0232	0·0274
II	0·0160	0·0190	0·0226	0·0280
I	0·0158	0·0194	0·0230	0·0284
IV	0·0162	0·0200	0·0220	0·0292
H_2O	0·0156	0·0192	0·0226	0·0286

Examination of the Colloidal Solutions.

In order to define the colloid systems employed and to facilitate re-examination, detailed investigations have been made into the chemical and physical properties of the colloidal solutions used, in the hope that from a consideration of the solubility phenomena and other properties, the intrinsic structures may perhaps be determined. The systems were investigated, therefore, from the point of view of (1) concentration, (2) density, (3) electrical conductivity, (4) depression of the freezing point, and (5) viscosity.

1. *Concentration.*—(a) *Prussian blue.* Gravimetric and volumetric analyses were made. The evaluation of the effective concentration met with some difficulty, owing to a certain quantity of peptising agent which was present in solution. This was avoided in the following way. A certain quantity of solution (5—10 g.) was heated and sodium hydroxide added until all the Prussian blue was converted into ferric hydroxide, which was filtered off. The filtrate was acidified with dilute sulphuric acid, and the sodium ferrocyanide titrated with $N/10$-potassium permanganate until the pink colour was permanent. From the quantity of permanganate used, the amount of $Fe(CN)_6'''$ ions which remained after the reaction with sodium hydroxide was easily calculated. There were also $Fe(CN)_6'''$ ions present from the beginning in the peptised solution, and for this reason the total $Fe(CN)_6'''$ found would give too large a

value for the Prussian blue content. To establish the exact quantity of the latter volumetrically, the ratio (φ) of $Fe(CN)_6'''$ formed from the Prussian blue to the total $Fe(CN)_6'''$ present was determined by gravimetric analysis of the precipitated ferric hydroxide. This was dissolved in dilute hydrochloric acid, re-precipitated with ammonia, and estimated as ferric oxide. The sodium ferrocyanide equivalent to the ferric oxide found was the amount of ferrocyanide obtained from the Prussian blue, which was thus directly determined. The value of φ could now be found—using the results with permanganate—and was calculated to be 0·9430. Since φ was constant (all solutions being of one preparation), all measurements of the concentration of Prussian blue could then be made by the permanganate method, which was therefore used. Both methods show a satisfactory agreement to within 0·1%, *e.g.*, solution I gave 3·91% volumetrically and 4·02% by the gravimetric method, and solution III, 7·368 and 7·362%, respectively.

(b) *Ferric hydroxide.* The concentration of this solution was determined from the amount of ferric oxide obtained on evaporating a definite quantity of the solution and heating the residue to redness. Considerable difficulty was experienced in determining the quantity of the peptising agent (acetic acid). In the first place, the ratio $Fe(OH)_3$: peptising agent was not constant, because the latter changed whenever the solution was boiled; and secondly, the quantity of acetic acid present was so small that direct titration could afford no exact results. Finally, about 30—40 g. of the solution were acidified with dilute sulphuric acid and about one litre of the resulting solution was distilled. The acetic acid in the distillate was neutralised with baryta, and the excess of this precipitated with carbon dioxide. The whole was concentrated to a small volume, the barium carbonate filtered off, and the barium acetate in the filtrate precipitated with sulphuric acid. The amount of acetic acid was calculated from the weight of barium sulphate found. The greater solubility of barium carbonate over barium sulphate was taken into consideration in the results, which are in Table XII.

2. *Density.*—Densities were determined with a large pyknometer, and the results compared with the density of water at 4° and reduced to vacuum values. Only the results actually obtained are in Tables XI and XII. The results show that, over the whole temperature range studied, density is a linear function of concentration.

3. *Electrical Conductivity.*—The object of these measurements was to determine to what degree the colloid was free from contamination by electrolytes; for an increase in conductivity might have been due to such contamination and eventually to colloidal

Table XI.

Concentration and Density, $Fe_4[Fe(CN)_6]_3$.

	Concentration.		Peptis., $Na_4[Fe(CN)_6]$.		Density.					
No.	Equiv. *N.*	%.	Equiv. *N.*	%.	30°.	25°.	20°.	15°.	10°.	5°.
H_2O†	—	—	—	—	0·9957	0·9971	0·9982	0·9991	0·9997	1·0000
4	0·126	0·94	0·008	0·06	—	1·0029*	1·0040	1·0049	1·0054*	1·0059
5	0·178	1·27	0·011	0·08	—	1·0055*	1·0066	1·0075	1·0081*	1·0086
II	0·250	1·788	0·016	0·12	1·0671	1·0085	1·0096*	1·0105	1·0111	—
3	0·37	2·64	0·022	0·17	—	1·0142*	1·0153	1·0162	1·0168*	1·0172
2	0·51	3·65	0·030	0·23	—	1·0213*	1·0224	1·0233*	1·0239	1·0242
I	0·546	3·91	0·033	0·25	1·0205*	1·0219	1·0230*	1·0238	1·0244*	—
1	0·896	6·41	0·053	0·40	—	1·0374*	1·0385	1·0394	1·0401*	1·0404
III	1·028	7·36	0·062	0·47	1·0427*	1·0442	1·0454*	1·0462	1·0467*	—

† Compare Landolt–Börnstein–Röth, *op. cit.*, p. 42.

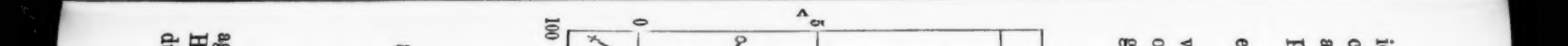
Table XII.

Concentration and Density, $Fe(OH)_3$.

	Concentration.		Peptisation, $CH_3{\cdot}COOH$.i		Density.					
No.	Equiv. *N.*	%.	Equiv. *N.*	%.	30°.	25°.	20°.	15°.	10°.	5°.
H_2O†	—	—	—	—	0·9957	0·9971	0·9982	0·9991	0·9997	1·0000
2	0·071	0·252	0·002	0·01	—	0·9982	0·9993	1·0002*	1·0008	1·0011
IV	0·12	0·425	—	—	0·9984	0·9998	1·0009	1·0018*	1·0024	—
1	0·144	0·514	0·0036	0·021	—	1·0002*	1·0014	1·0023*	1·0027*	1·0030
4	0·293	1·042	0·003	0·017	—	1·0037*	1·0048	1·0057	1·0063*	1·0066
I	0·336	1·196	—	—	1·0031*	1·0046	1·0057*	1·0066	1·0072*	—
3	0·513‡	1·825	0·0096	0·057	—	1·0087*	1·0098	1·0106	1·0112*	1·0115
II	0·521	1·875	—	—	1·0075*	1·0089	1·0100*	1·0109	1·0114*	—
III	0·871	3·103	—	—	1·0157	1·0171	1·0182	1·0191*	1·0197	—
5	0·967	3·446	0·011	0·064	—	1·0191*	1·0202	1·0211	1·0218*	1·0221

† Compare Landolt–Börnstein–Roth, *op. cit.*, p. 42.
‡ This number is obtained from a density determination.

The values marked * in Tables XI and XII were obtained experimentally, the others by interpolation.



ions. Moreover, the questions arise (1) to what extent is peptisation changed by the action of the colloidal solution, and (2) are ionisation and ionic mobility much the same, at similar concentrations, as in a pure solvent?

The Kohlrausch method, with inductor and telephone, was employed and the results are in the following tables and diagrams.

(a) *Prussian Blue* (see Table XIII and Fig. 6). All measurements were made at 18°. For purposes of comparison the conductivity of pure sodium ferrocyanide is given in Table XIV and shown graphically in Fig. 7.

FIG. 6.

Prussian blue.

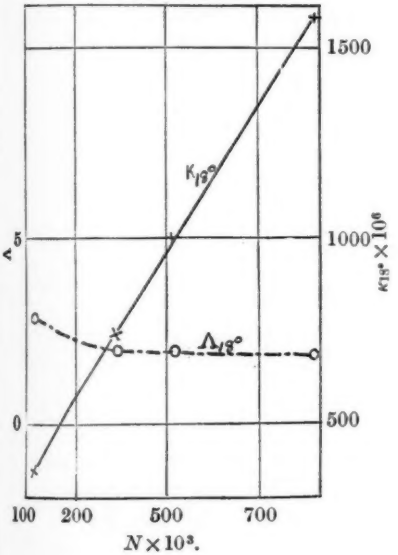


FIG. 7.

Sodium ferrocyanide.

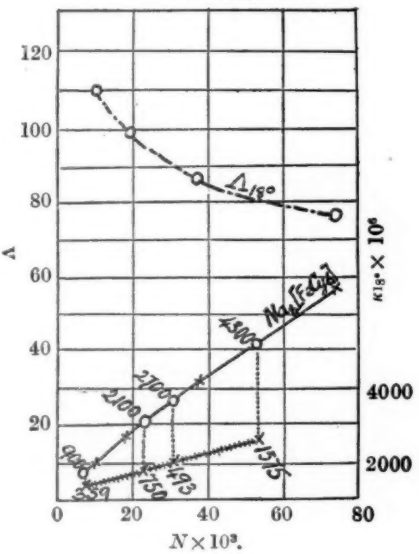


TABLE XIII.

Prussian blue.

Soln.	$N \times 10^3$.	$\kappa_{18°} \times 10^6$.	$\Lambda_{18°}$.
1	896	1575·0	1·75
2	510	992·6	1·94
3	370	750·0	2·03
4	126	359·4	2·85

TABLE XIV.

$Na_4Fe(CN)_6$.

$N \times 10^3$.	$\kappa_{18°} \times 10^6$.	$\Lambda_{18°}$.
74	5664	76·6
37	3205	86·8
18·5	1803	97·5
9·3	1000	110·0

$\Lambda = \kappa \times 10^6 / N \times 10^3$.

A remarkable feature of Fig. 7 is that the curve for the peptising agent in the solution lies below that of the ferrocyanide in water. Hence it was assumed that the conductivity of the colloid was wholly due to the amount of peptising agent present, and therefore the

The values marked * in Tables XI and XII were obtained experimentally, the others by interpolation.

abscissæ of the lowest curve in the figure are those of the peptising agent in Prussian blue solution : the ordinates are corresponding values of equivalent conductivity of Prussian blue. The values are taken from Table XIII. The continuations of these ordinates cut the curve for sodium ferrocyanide in water, and the data at these points of intersection show the conductivities of a pure solution of sodium ferrocyanide of the same concentration as in the colloid. The conductivity curve for sodium ferrocyanide with peptisation

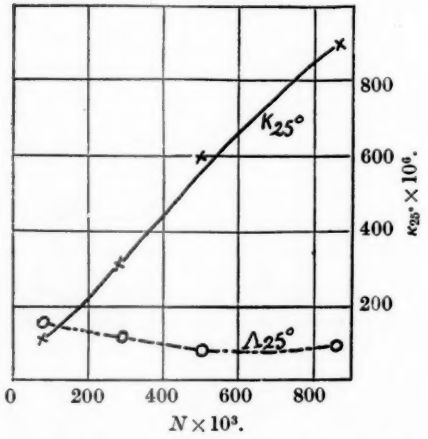
TABLE XV.

$Fe(OH)_3$.

Soln.	$N \times 10^3$.	$\kappa_{25°} \times 10^6$.	$\Lambda_{25°}$.
2	71	104·6	1·511
1	144	238·0	1·641
4	293	314·3	1·073
3	513	508·5	1·741
5	967	903·0	0·934

FIG. 8.

Ferric hydroxide.



is a straight line, and the gradient of this line with respect to the curve for sodium ferrocyanide in water is about 0·368. Hence the ordinates, y_1, of the one curve are constant multiples of the ordinates, y_2, of the other, *i.e.*, $y_1 = \text{constant} \times y_2$. It would be of interest to investigate the behaviour of other colloids in a similar way.

(b) *Ferric hydroxide* (see Table XV and Fig. 8). All the measurements were made at 25°. The curve for equivalent conductivity seems to pass through a minimum at a normality of about 0·5. The equation, $y_1 = y_2 \times$ constant, found for Prussian blue, unfortunately, cannot be examined in this case, for the conductivity of

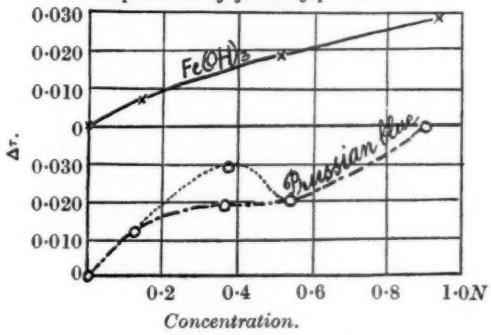
this colloid is far superior to that of the peptising agent—if this alone is considered—as the following data show :

Acetic acid.		Coll. $Fe(OH)_3$.		
			Peptisation	
$N \times 10^3$.	$\kappa_{25°} \times 10^6$.	No.	$(N \times 10^3)$.	$\kappa_{25°} \times 10^6$.
2	67	2	2	105
5	110	4	3	314
10	158	3	9·6	509
20	229	5	11·0	903

The figures in this table show that ions of acetic acid—and it may be others as well—transport electric charges. These others, especially chlorine ions, may arise from impurities adsorbed by the ferric hydroxide when it was first precipitated and irremovable by washing. The discussion which follows later shows that the

FIG. 9.

Depression of freezing-point.



greater conductivity of these solutions of ferric hydroxide may possibly be due to " colloidal ions."

4. *Depression of Freezing-point.*—These determinations, which were carried out in a Beckmann apparatus, were made in order to estimate, as far as possible, the relative numbers of particles in the solutions and also to determine whether these numbers vary proportionally to the concentration. The results are in Table XVI (see also Fig. 9).

TABLE XVI.

Freezing-point Depression, $\Delta\tau$.

Prussian blue.			Ferric hydroxide.		
Soln.	Conc. (N).	$\Delta\tau$.	Soln.	Conc. (N).	$\Delta\tau$.
1	0·896	0·040°	5	0·967	0·029°
2	0·51	0·020	3	0·513	0·018
3	0·37	0·030** 0·019**	1	0·144	0·008
4	0·126	0·012			

A small freezing-point depression is an indication of the comparative purity of a colloidal system. The values marked ** in the table were obtained at different times and the value 0·030 was constant. The curve may possibly rise to a maximum for a concentration of 0·3N, or there may here be a point of inflexion if the lower and more probable value, 0·019, be plotted.

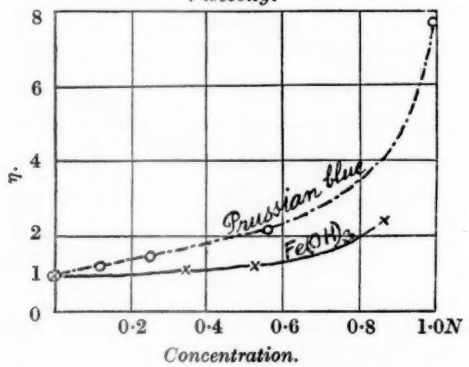
TABLE XVII.

Viscosities at 25°.

Ferric hydroxide.				Prussian blue.			
Soln.	s.	t (secs.).	η.	Soln.	s.	t (secs.).	η.
H_2O	0·9960	62·8	1·000	H_2O	0·9960	62·8	1·000
2	0·9982	63·7	1·017	4	1·0029	73·0	1·170
I	1·0046	67·8	1·089	II	1·0085	84·4	1·361
II	1·0089	72·0	1·161	I	1·0219	128·8	2·104
III	1·0171	150·6	2·448	III	1·0442	446·7	7·452

FIG. 10.

Viscosity.



The molecular weights of ferric hydroxide calculated from the results are 2240, 2000, and 1090 for solutions 5, 3, and 1, respectively. These values, of course, carry little weight, but they seem to indicate that with increasing concentration the particles in the solution coalesce to form larger aggregates.

5. *Viscosity.*—These measurements were made because there may be an intimate relation between the viscosity of a colloidal solution and its absorptive power. The apparatus, an Ostwald viscosimeter, was in a large thermostat at 25° and, as usual, two series of experiments were made. The viscosities were calculated by means of the equation $\eta = \eta_W \cdot st/s_W t_W$, where η and η_W are the relative viscosities of the solution and water, respectively, s is the density of the solution and t is the time of flow. The results are in Table XVII and are shown graphically in Fig. 10.

Discussion of Results.

An examination of the solubility tables reveals the very different behaviour of the two colloidal solutions towards carbon dioxide and acetylene.

The solubility of carbon dioxide in the more concentrated solutions of ferric hydroxide exceeds its solubility in water by as much as 20%. Moreover, it is almost directly proportional to the concentration—a relation found by Findlay also (*loc. cit.*), although his absolute values of l were considerably smaller than those now recorded.

Carbon dioxide is also more soluble in solutions of Prussian blue than in water, but only moderately so (at the most, 3—4%). A well-defined maximum occurs in the values of l at all the temperatures used, in every case at a concentration of 0·3-normal.

Towards acetylene, however, both colloidal solutions display an essentially different behaviour, the solubility of the gas being always less than its solubility in water. The diminution is 1% for ferric hydroxide and 7—8% for Prussian blue (compare Findlay's curves, reproduced in Fig. 5, for nitrous oxide in ferric hydroxide at 25°).

For these colloidal systems the relation between the solubility of gases and the temperature is in accord with the ordinary laws governing the solution of gases, *viz.*, the temperature coefficient is negative and its numerical value increases rapidly with diminishing temperature (see Table VIII). This magnitude appears to be a function of concentration (at constant temperature). The following rule, therefore, may be deduced. At a given temperature, the numerical value of the temperature coefficient varies, with increasing concentration, as the absorptive power of the colloidal solution for the dissolving gas. For instance, in the system carbon dioxide–ferric hydroxide, l increases rapidly with c and consequently the quotient $\Delta l/\Delta t$ increases as c increases: or, in the system acetylene–ferriferrocyanide, l diminishes greatly as c increases, and consequently $\Delta l/\Delta t$ decreases as c increases. Such behaviour, however, is not so well defined in the systems carbon dioxide–ferriferrocyanide and acetylene–ferric hydroxide, since l varies but little. In the latter case, a diminution even of the temperature coefficient might be assumed owing to the small diminution of l.

The factors which may account for the observed phenomena are (1) the chemical nature of the colloid and of the gas absorbed (chemical combination), (2) the influence of the specific surface (adsorption), (3) the nature of the electric change, and (4) temperature.

1. *Chemical nature.* This is, presumably, the most important factor in all absorption phenomena, but, unfortunately, it is still

very obscure. Clearly, the more inert the gas and the colloidal solution are chemically, the smaller will be the effect of this factor. An obvious conclusion from this is that l for the systems carbon dioxide–Prussian blue and acetylene–ferric hydroxide will differ but little from the value of l for water, since fairly inert substances meet each other. On the other hand, a chemical reaction may be expected to take place between the basic ferric hydroxide and the acidic carbon dioxide. It is true that there is as yet no evidence of the existence of a compound $Fe_2(CO_3)_3$. Since, however, electropositive ferric hydroxide, according to Pauli and Mattula (*Kolloid-Z.*, 1917, **21**, 49), has the constitution $[x\mathrm{Fe(OH)_3}]y\mathrm{Fe}^{\cdots}$, and there is formed by the dissociation of the dissolved carbon dioxide a small amount of CO_3'', a combination of this with the tervalent iron to give complex colloidal $\{[x\mathrm{Fe(OH)_3}]y\mathrm{Fe}\}_2(y\mathrm{CO_3})_3$ may reasonably be assumed. This assumption seems to be justified by the strikingly high conductivity of the colloidal solution, which far exceeds that due to the peptising agent present.

2. *Specific surface.* The present results, as well as those of Geffcken and Findlay, clearly show that some factor is operating in addition to adsorption. The extent of the latter is determined by the degree of dispersion, and to account for the different behaviour of the two colloids by adsorption alone the specific surface of the ferric hydroxide would have to be 8—10 times larger than that of the Prussian blue—an assumption that cannot be justified.

Dispersion, however, has an effect, and to determine it the absorption of carbon dioxide for different dispersions of ferric hydroxide at the same concentration (0·066N) was measured.

Values of l.

	25°.	20°.	15°.	10°.
High dispersion	0·854	0·961	1·095	1·268
Low dispersion	0·817	0·930	1·068	1·239
Water	0·826	0·936	1·070	1·240

At the higher temperatures the absorptive power of the less highly dispersed system is markedly depressed, even below that of water. This diminution, however, depends not only on the specific surface of the colloid, but also on the quantity of peptising agent present. In the less highly dispersed system this was 0·3% and the basic character of the ferric hydroxide was greatly diminished and its electrical nature correspondingly changed.

3. *Electric change.* The changes that take place when carbon dioxide is in contact with a colloidal solution of ferric hydroxide may be represented by the following scheme; for a given temperature and pressure a definite equilibrium will be set up :

(1) $Fe(OH)_3 \rightleftharpoons Fe''' + 3(OH)'$.

(2) $H_2CO_3 \rightleftharpoons CO_3'' + 2H^{\cdot}$.

(3) The colloidal particles become associated with Fe''': $[xFe(OH)_3] + yFe''' \longrightarrow [xFe(OH)_3]yFe'''$.

(4) $H^{\cdot} + OH' \rightleftharpoons H_2O$.

(5) $2[xFe(OH)_3]yFe''' + 3yCO_3'' \rightleftharpoons \{[xFe(OH)_3]yFe\}_2\ (yCO_3)_3$ (compare Pauli and Mattula, *loc. cit.*).

The remarkably high solubility of carbon dioxide in ferric hydroxide and the readiness with which the gas is expelled by heating may thus be explained.

The preceding explanation involves the basic character of ferric hydroxide, the positive charge on the colloidal particles, and the acid nature of the gas. The last factor may for all practical purposes be neglected in the case of acetylene and nitrous oxide. Geffcken (*loc. cit.*, p. 301) has shown the indifferent nature of nitrous oxide by conductivity determinations with saturated aqueous solutions. The following measurements, made by the author, reveal the slight increase in conductivity that occurs when water is saturated with acetylene: water $2{\cdot}18$, $2{\cdot}81$, $2{\cdot}94 \times 10^{-6}$; mean $2{\cdot}63 \times 10^{-6}$. Water saturated with acetylene $5{\cdot}64$, $4{\cdot}98$, $4{\cdot}03 \times 10^{-6}$; mean $4{\cdot}88 \times 10^{-6}$. This result is in agreement with the investigations of Billitzer (*Z. physikal. Chem.*, 1902, **40**, 535), who pointed out a very slight dissociation of acetylene, represented by the following scheme,

$$C_2H_2 \longrightarrow C \equiv C'' + 2H^{\cdot} \mid C_2H_2 \longrightarrow C_2H' + H^{\cdot}$$

and found that the gas in saturated aqueous solution at atmospheric pressure corresponds to an acid about 400 times weaker than carbonic acid. Acetylene, therefore, and nitrous oxide may be regarded as inert gases, and their similar behaviour towards ferric hydroxide is thus satisfactorily explained. It is chiefly absorption that takes place, and this accounts, to some extent at least, for the diminution of solubility which occurs with increasing concentration. The large decrease of l for the system acetylene–Prussian blue is attributable to the high concentration of the colloid (above 7%), in comparison with that of the ferric hydroxide (3%), and to its negative charge.

4. *Temperature.* The rule stated on p. 313 may be explained on the basis of the kinetic theory. If the solubility increases with the concentration, the content both of colloid and of gas particles in the solution also increases and the conditions for the presence of gas particles become less favourable; so the rate of diminution of solubility per 1° rise in temperature becomes greater. A decrease in solubility with increasing concentration favours the retention of the gas particles in the solution: hence the diminished quantity

of gas corresponding with 1° may be expected to remain constant or even to fall.

Summary.

1. Two typical, highly concentrated colloidal solutions have been prepared, and a very highly dispersed system of ferric hydroxide has been obtained by a modification of P. de St. Gilles's method.

2. Measurements of the solubility of carbon dioxide and acetylene in these systems have been made at five temperatures and different concentrations, and the temperature coefficients determined.

3. The colloids have been characterised by determinations of density, concentration, conductivity, viscosity, and depression of freezing-point.

4. Certain regularities in solubility have been found and an attempt has been made to analyse the factors that produce them.

The author wishes to express his thanks to Dr. Charles Brunner, and to acknowledge his indebtedness to the late Dr. Chas. Hopfgartner, at whose suggestion the work was undertaken.

INNSBRUCK,
SILLGASSE, 2. [*Received, July 18th*, 1925.]

XL.—*The Reciprocal Salt Pair* (Na, Ba)–(Cl, NO_3) *in Aqueous Solution at* 20°.

By ALEXANDER FINDLAY and JAMES CRUICKSHANK.

THE investigation of this system was undertaken with a view to ascertain the best conditions for the preparation of barium nitrate from the chloride by interaction with sodium nitrate. The most important equilibria were investigated by one of us in 1917, and the further investigation of the system was taken up later with the intention of completing the equilibrium data at 20° and of extending the study also to higher temperatures. This extension of the investigation, however, has been rendered unnecessary by the work of Coppadoro (*Gazzetta*, 1912, **42**, 1; 1913, **43**, 138). We have restricted ourselves, therefore, to an examination of the equilibria at 20°.

The following values have been determined for the composition of aqueous solutions in equilibrium with one, two, and three salts, respectively, included in the above reciprocal salt pair.

1. Single salts.

Solid phase.	G. of anhydrous salt in 100 g. of soln.	Solid phase.	G. of anhydrous salt in 100 g. of soln.
NaCl	26·40	$BaCl_2,2H_2O$	26·32
$NaNO_3$	46·77	$Ba(NO_3)_2$	8·41

2. System $NaCl–BaCl_2–H_2O$.

Solid phase.	Percentage composition of solutions. NaCl.	$BaCl_2$.	H_2O.
NaCl	25·28	1·65	73·07
NaCl; $BaCl_2,2H_2O$	24·59	3·07	72·34
$BaCl_2,2H_2O$	21·23	4·17	74·60
,,	18·52	6·51	74·97
,,	14·50	10·04	75·46
,,	9·54	14·99	75·47
,,	7·80	16·89	75·31

3. System $NaCl–NaNO_3–H_2O$.

Solid phase.	Percentage composition of solutions. NaCl.	$NaNO_3$.	H_2O.
NaCl	18·49	18·62	62·89
,,	17·34	21·30	61·36
NaCl; $NaNO_3$	13·80	30·34	55·86
$NaNO_3$	9·56	34·85	55·58
,,	7·67	37·18	55·15

4. System $BaCl_2–Ba(NO_3)_2–H_2O$.

Solid phase.	Percentage composition of solutions. $BaCl_2$.	$Ba(NO_3)_2$.	H_2O.
$BaCl_2,2H_2O$	26·07	1·31	72·62
$BaCl_2,2H_2O$; $Ba(NO_3)_2$	25·09	6·93	67·98
$Ba(NO_3)_2$	20·81	6·54	72·65
,,	12·31	6·72	80·97
,,	7·51	7·17	85·32

5. System $NaNO_3–Ba(NO_3)_2–H_2O$.

Solid phase.	Percentage composition of solutions. $NaNO_3$.	$Ba(NO_3)_2$.	H_2O.
$NaNO_3$; $Ba(NO_3)_2$	45·74	1·86	52·40
$Ba(NO_3)_2$	37·07	2·07	60·86
,,	14·59	2·49	82·92
,,	5·61	3·89	90·50

6. Quaternary Solutions.

Solid phase.	Percentage composition of solutions. NaCl.	$NaNO_3$.	$Ba(NO_3)_2$.	$BaCl_2$.	H_2O.
$NaNO_3$; $Ba(NO_3)_2$	6·57	37·82	1·62	—	53·99
NaCl; $Ba(NO_3)_2$	15·79	24·08	0·14	—	59·99
$BaCl_2,2H_2O$; $Ba(NO_3)_2$	2·02	—	6·49	22·66	68·83
NaCl; $Ba(NO_3)_2$; $NaNO_3$	14·23	29·75	0·13	—	55·89
NaCl; $Ba(NO_3)_2$; $BaCl_2,2H_2O$	24·16	0·50	7·14	—	68·20

The last noted solution is incongruently saturated.

For the practical application of the above determinations, the following numbers are of interest :

Initial composition of mixture (g. of anhydrous salt per 1000 g. of water). $NaNO_3$.	$BaCl_2$.	Percentage of salt precipitated as $Ba(NO_3)_2$. $BaCl_2$.	$NaNO_3$.
283	337·8	76·45	74·45
471·8	337·8	92·55	54·06

It will, in general, be advantageous to use a relatively large proportion of sodium nitrate in the initial mixture so as to obtain as complete a utilisation as possible of barium chloride. The mother-liquor containing sodium nitrate can be used, after evaporation and separation of the sodium chloride, for the conversion of a further quantity of barium chloride.

UNIVERSITY OF ABERDEEN. [*Received, December 31st*, 1925.]

XLI.—*The Equilibrium between Ethyl Alcohol and the Alkali and Alkaline-earth Salts. Part I.*

By DAVID GLYNWYN ROBERT BONNELL and WILLIAM JACOB JONES.

THE first investigator in this field was Graham (*Phil. Mag.*, 1828, **4**, 265, 331), who prepared the ethyl alcoholate of calcium chloride. His work was repeated by Einbrodt (*Annalen*, 1848, **65**, 115), by Chodnew (*Bull. Acad. St. Petersburg*, 1865, **8**, 150), by Heindl (*Monatsh.*, 1881, **2**, 200), and by Menschutkin (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 1010). The calcium bromide tri-alcoholate (Roques, *J. Pharm.*, 1895, **1**, 301), the hexa-alcoholates of magnesium chloride (Simon, *J. pr. Chem.*, 1879, **20**, 371), bromide and iodide (Menschutkin, *Bull. St. Petersburg Polytec. Inst.*, 1906, **3**, 12), the tetra-alcoholates of lithium chloride (Simon, *loc. cit.*) and bromide (Turner and Bissett, J., 1914, **105**, 1783) have all been described. Solubility determinations over ranges of temperatures have been carried out as follows: lithium chloride (Turner and Bissett, J., 1913, **103**, 1904), sodium and potassium iodides (Tyrer, J., 1910, **97**, 621) and calcium chloride (Menschutkin, *loc. cit.*).

The purpose of the present series of investigations was to determine the following: (1) The solubility over a wide range of temperature. (2) The composition of the various solid phases. (3) The transition temperatures. In the present paper are described the conditions of equilibrium between ethyl alcohol and the following salts: lithium bromide, sodium bromide, calcium bromide, barium bromide, and barium iodide.

EXPERIMENTAL.

For obvious reasons great attention was directed to the purity of the substances used, and especially to their freedom from traces of water, since, owing to the far greater affinity of salts for this than for alcohol, the composition of the solid phase is particularly influenced by its presence.

The alcohol was purified by Lapworth's method (J., 1910, **97**, 24).

The densities, without correction of the weighings to vacuum, of the two specimens that were used in the present work were $d_4^{25°}$ 0·78494 and 0·78496. Great care was exercised both during the purification and preservation and in subsequent work to exclude atmospheric moisture.

The salts were purified by recrystallisation from water and then dehydrated by Turner and Bissett's method (P., 1913, **29**, 233) (Found by the gravimetric silver halide method: LiBr 99·81, NaBr 99·93, $CaBr_2$ 99·90, $BaBr_2$ 99·89, BaI_2 99·87%).

The graduated vessels, weights and thermometers had been carefully standardised. In the solubility determinations above 20° ordinary thermostats, which kept constant within 0·02°, were used. At 15° and at 10°, the temperature was maintained constant within 0·04° by a regulated inflow of cold water and by continuous and vigorous stirring. For 0°, a bath of washed, finely powdered ice was used. In each determination the anhydrous salt and alcohol were put together in a clean, dry, glass-stoppered flask, which thereafter was kept in the thermostat, and as far as possible in the dark. A tightly fitting, thick paper cap was tied over the stopper. The mixtures were shaken by hand at intervals over a long period, and a portion of the solution was then withdrawn for analysis after the solid had settled completely. Thereafter the mixtures were again shaken and the procedure described was repeated until two consecutive analyses agreed within the experimental error. By operating in this manner saturation was ensured and incursion of atmospheric moisture was better precluded than if an internal stirring arrangement had been used. In some of the experiments, the equilibrium point was approached by first preparing a saturated solution at a temperature at which the solubility was greater than at the temperature under investigation, then placing it in the thermostat at the latter temperature, and, after keeping it therein for some time with frequent shaking, analysing the liquid phase. In all cases, the solubility so found was identical with that found by the procedure previously described. There can therefore be no doubt that in our experiments the systems were truly in equilibrium when the solubility determinations were made.

For the determination of the composition of the solid phase a small quantity was scooped out, quickly dried between filter-paper, and analysed. For such solid phases as were stable only at temperatures much above the ordinary, the procedure was modified as follows. Some of the salt was suspended by means of a basket of metal gauze in a saturated solution in a stoppered flask, which was immersed in the thermostat. When equilibrium had been attained, the basket was drawn up into the vapour space above the solution

and was there allowed to drain. When draining was complete, the solid in the basket was withdrawn and analysed.

The transition temperatures obtained by the solubility determinations were confirmed by the dilatometric method.

Results.

Solubility in gram of salt per gram of alcohol, of

Temp.	sodium bromide.	barium bromide.	barium iodide.	calcium bromide.	lithium bromide.
0°	0·02445	0·05880	0·7775	0·4670	0·3261
10	0·02379	0·05067	0·7735	0·4801	0·3602
15	0·02343	0·04590	—	0·5051	—*
20	0·02322	0·04130	0·7700	0·5350	—*
25	0·02314	—	—	0·5395	0·7210
30	0·02292	0·03322	0·7660	0·5552	0·7251
40	0·02276	0·02433	0·7620	0·6011	0·7303
50	0·02259	0·01837	0·7585	0·6564	0·7752
60	0·02312	0·01479	0·7550	0·7602	0·8284
70	0·02345	0·01253	0·7510	0·9381	0·8913
75	—	—	—	1·0220	0·9412
80	—	—	—	1·0310	0·9910
85	—	—	—	1·0610	—

* Retroflex region (see later table).

All the above values were determined directly.

Throughout in the cases of sodium bromide, barium bromide, and barium iodide the solid phases were respectively NaBr, $BaBr_2$, and BaI_2.

In the case of calcium bromide, below 17·0° the solid phase is $CaBr_2,4C_2H_5{\cdot}OH$, between 17·0° and 73·9° $CaBr_2,3C_2H_5{\cdot}OH$, and above 73·9° $CaBr_2,C_2H_5{\cdot}OH$ ($CaBr_2,4C_2H_5{\cdot}OH$: ethyl alcohol found, 48·6; calc., 48·0%. $CaBr_2,3C_2H_5{\cdot}OH$: ethyl alcohol found, 42·4; calc., 40·9%. $CaBr_2,C_2H_5{\cdot}OH$: ethyl alcohol found, 20·5; calc., 18·7%). The form of the solubility curves exhibits a close parallelism to those of calcium chloride in water and in methyl alcohol.

When lithium bromide and alcohol were brought together, great heat was developed and a solution of a slightly brown tint was obtained. At 25° and 30° the solution was very viscous, and consequently took a long time to settle sufficiently to allow of measurements being taken. In the temperature range 13·2° to 23·8° there is a retroflex region, the solid phase being $LiBr,4C_2H_5{\cdot}OH$ (ethyl alcohol found, 69·2; calc., 67·9%). The congruent melting point of the tetra-alcoholate was 23·8°, and the solid phase in contact with the saturated solution at the higher temperatures has the composition LiBr. The eutectic point for the anhydrous salt and the alcoholate is 13·2°. The alcoholate crystallises in flat plates which are highly deliquescent in the atmosphere, and, owing to the

hygroscopicity of the salt, it was impracticable to determine its affinity for alcohol. Greater detail regarding the eutectic region is given in the following table :

Retroflex Region of the Solubility of Lithium Bromide in Ethyl Alcohol.

	Solubility in gram of lithium bromide per gram of ethyl alcohol with solid phases.		
Temp.	LiBr.	$LiBr,4C_2H_5\cdot OH$.	$LiBr,4C_2H_5\cdot OH$.
13·2°	0·700	0·700	0·700
15·0	0·702	0·687*	0·381
16·0	0·704	0·675*	0·390
20·0	0·708	0·606*	0·420
23·0	0·712	0·530*	0·460
23·8	0·713	0·472	0·472

The asterisked values were obtained by thermal analysis, the remaining values being obtained either by direct determinations of solubility or from a graph.

When the barium iodide was brought into contact with the alcohol great heat was developed, and in a short time the solution acquired an orange tint due to the presence of traces of free iodine. A fresh solution was made in a black flask, but even in this the colour again developed and it was found impossible to obtain colourless solutions.

UNIVERSITY COLLEGE, CARDIFF. [*Received, November 28th*, 1925.]

XLII.—*The Dissociation Pressures of Alcoholates. Part I.*

By DAVID GLYNWYN ROBERT BONNELL and WILLIAM JACOB JONES.

No account of work on this subject has yet been published, and because of its importance in relation to the affinity of salts for the alcohols and to residual affinity in general, we have undertaken the present investigation.

The methods, which are applicable in the case of hydrates, may be divided into the following classes : (*a*) indirect, (*b*) tensimetric, and (*c*) dynamical, or gas current saturation. In the following, the applicability of each method is discussed.

Among indirect methods are those of Müller-Erzbach (*Ber.*, 1881, **14**, 1093; *Z. physikal. Chem.*, 1888, **2**, 113), Wilson (*J. Amer. Chem. Soc.*, 1921, **43**, 704), Lescœur (*Ann. Chim. Phys.*, 1889, **16**, 378; 1890, **19**, 533), Cumming (J., 1909, **95**, 1772), Linebarger (*Z. physikal. Chem.*, 1894, **13**, 500), Foote and Scholes (*J. Amer. Chem. Soc.*, 1911, **33**, 1309), and Noyes and Westbrook (*ibid.*, 1921, **43**, 726). Müller-Erzbach employed two methods. In the first,

he compared the rates of diffusion of aqueous vapour from water and from the hydrate. His second method was to find the dilution of aqueous sulphuric acid solution over which the hydrate neither gained nor lost weight, and, when this was the case, the dissociation pressure was equal to the known aqueous pressure of the acid solution at the temperature of the experiment. Wilson's method is identical in principle with the latter method of Müller-Erzbach. This method might be made applicable to alcoholates if, first, the aqueous sulphuric acid were replaced by an alcoholic solution of a difficultly volatile substance and, secondly, the alcoholic vapour pressures of solutions of various concentrations of this substance in alcohol had been previously determined at various temperatures. The time required for such an investigation might, however, be prohibitive. Both Lescoeur and Cumming determined the dew point of the vapour phase in equilibrium with the pair of hydrates. Their method is directly applicable to the alcoholates, but, where the dissociation pressure is low, suffers from the disadvantage that the steep gradient of temperature in the apparatus introduces a serious source of error. Linebarger found the aqueous vapour pressure of a pair of salt hydrates, at the boiling point of ether, by determining the boiling point of the moist ether in contact and equilibrium with them, and then referring to a table giving the boiling points of various aqueous ether mixtures and their partial aqueous vapour pressures at those temperatures. Foote and Scholes shook a mixture of two hydrates with alcohol, and, after the attainment of equilibrium, determined the water content of the alcoholic layer. The dissociation pressure of the hydrate at the temperature of the experiment is equal to the known partial pressure of a water–alcohol mixture of the same composition as this layer. Noyes and Westbrook have employed a method which in principle is identical with that of Foote and Scholes, the reference liquid used being *iso*-amyl alcohol. In the latter three methods, the properties of the reference liquids are so strictly circumscribed that it would be difficult to find a suitable liquid for use in the investigation of the alcoholates. Thus the salt must be insoluble in the reference liquid, the reference liquid must not form stable solid solvates with the salts in the presence of the alcohols, its affinity for the alcohols must be negligible compared with that of the salts for alcohol, and it must be only partly miscible with alcohol.

In order to apply the tensimetric method of Frowein (*Z. physikal. Chem.*, 1887, **1**, 1, 362), a liquid in which the alcohols are insoluble has to be employed in the manometer, and mercury, which is the only practicable liquid, is so dense that accuracy cannot be conveniently attained by its use. Moreover Menzies (*J. Amer. Chem. Soc.*, 1920,

42, 1952) has found that it is extremely difficult to evacuate the tensimeter satisfactorily.

The dynamical method, which is originally due to Tammann (*Ann. Physik*, 1888, **33**, 329), has been elaborated and perfected for the hydrates by Partington (J., 1911, **99**, 466), Baxter and Lansing (*J. Amer. Chem. Soc.*, 1920, **42**, 419), Partington and Huntingford (J., 1923, **123**, 160), Schumb (*J. Amer. Chem. Soc.*, 1923, **45**, 342), and Baxter and Cooper (*ibid.*, 1924, **46**, 923). We have found that this method is eminently suited to the investigation of the dissociation pressures of the alcoholates.

Two objections have been urged against this method, namely, first, that equilibrium is approached only from the side of undersaturation of the air current, and, secondly, that attainment of equilibrium between vapour phase and crystals is so slow that the time allowed in the passage of the air over the solid is insufficient. The first objection is disposed of by the data in Table I, where some experiments are detailed in which the equilibrium was approached both from undersaturation and from supersaturation, with results which within experimental error are identical. The second objection can be met only by ensuring that the rate of passage of air employed in the experiments is sufficiently slow, and by demonstrating that the same value is obtained for the dissociation pressures when a considerably slower rate is employed. The necessary slowness of the current depends, among other things, on the nature of the solvent, the salt, the temperature, and the dimensions of the saturator used. In our experiments the passage of 100 c.c. per hour gave the same result as that obtained with 500 c.c. per hour, and these were the extreme rates used. Furthermore, the fact that in our experiments air which was initially supersaturated with alcohol vapour gave the same result as air which was initially dry proves that the air leaving the saturator was adequately saturated with alcohol vapour and that a true state of equilibrium was attained.

Experimental.

The method adopted in the present work consisted in drawing a measured volume of dry air, free from carbon dioxide, through an intimate mixture of the pair of alcoholates, and finding the weight of alcohol vapour taken up by the air, either by collecting the alcohol in weighed U-tubes containing phosphorus pentoxide, or by determining the loss of weight of the mixture. The air, which was drawn through the mixture of alcoholates by means of an aspirator, was purified by passage in succession through concentrated sulphuric acid, a large calcium chloride tower, a U-tube filled with broken sticks of potassium hydroxide, and finally a 210 cm. train of freshly

prepared phosphorus pentoxide powder mixed with glass wool. The purified air passed into the saturator, which was similar in form to that used by Partington (J., 1911, **99**, 468, Fig. 1A), except that our U-tubes were sealed off instead of being closed with paraffined corks. The saturator was filled to the level of the side tube with a mixture of the pair of alcoholates under investigation. The diameter of the column of mixture was 2 cm. and its mean length 42 cm. The saturator was immersed in a thermostat with only the side tubes emergent. A differential mercury manometer attached to the exit side tube served to give the difference in pressure between the external atmosphere and the mixture of air and alcohol vapour as it left the saturator, and consequently the sum of the partial pressures of the alcohol and air could be found. The saturated air afterwards passed into a U-tube filled with phosphorus pentoxide mixed with glass wool, whereby it was deprived of its alcohol. All connexions in this part of the apparatus were made with tightly fitting rubber tubing, inside which the ends of the glass tubes were brought into contact with each other. The air next passed into a U-tube filled with calcium chloride, which served as a trap to prevent back-diffusion of moisture from the aspirator in which the air was finally collected. At the beginning of the experiment the aspirator was filled to the top with water, which had been allowed to come to room temperature before the air current was started. The air inlet tube reached practically to the bottom of the water in the aspirator, and the air acquired the temperature of the aspirator during its passage downwards through the inlet tube and upwards through the water to the top of the aspirator, where it collected. The volume of air passed over the alcoholates was found by weighing the water expelled from the aspirator. The temperature of the room was maintained constant. An open-limb differential mercury manometer served to give the difference in pressure between the air collected inside the aspirator and the external atmosphere.

Care was taken that the dry air always entered the saturator at the same end in order that the air leaving the saturator should always come into contact with a mixture of both solid phases. Similar care was taken with the phosphorus pentoxide tube in order to retain all traces of alcohol. Atmospheric moisture was rigorously excluded in the preparation of the alcoholates, and in their transfer to the saturator, which had been previously thoroughly dried by a current of hot air.

The alcoholic dissociation pressure, p, of the pair of alcoholates under investigation at the temperature of the thermostat is given in mm. of mercury by the equation $p/p' = v/(V + v)$, where v and V are the respective volumes of alcohol vapour and dry air in the

mixture leaving the saturator at the temperature of the experiment and under the pressure p', which is the sum of the partial pressures of the alcohol vapour and air as they leave the saturator, expressed in mm. of mercury. Since we are dealing with a ratio of volumes, the ratio of the pressures is unaltered if we substitute the values of the volumes at *N.T.P.*, which can be determined as follows :

$$v = \frac{22410m}{M}; \quad V = \frac{273{\cdot}1(P-f)W}{(273{\cdot}1+t)760d'}$$

wherein m is the mass of alcohol in grams lost from the saturator and M is the molecular weight of the alcohol, P is the final pressure of the air inside the aspirator, f is the aqueous vapour pressure at the temperature, $t°$, of the aspirator, both pressures being expressed in mm. of mercury, W is the mass in grams in a vacuum of the water expelled from the latter, and d its density.

$$\text{Thus } p = \frac{22410 \times 760(273{\cdot}1+t)p'md}{273{\cdot}1 \times WM(P-f) + 22410 \times 760(273{\cdot}1+t)md}.$$

P is determined by taking the barometer reading at the end of the experiment and subtracting therefrom the reading of the aspirator manometer.

The sum of the partial pressures, p', is equal to the average barometric pressure during the run minus the average value of the readings of the mercury manometer attached to the exit tube of the saturator.

The mass, m, of the alcohol lost by the saturator was found either by the increase in weight of the phosphorus pentoxide tube or by the decrease in weight of the saturator, or by both means. In these weighings suitable counterpoises were employed. Both methods agreed, as is shown in the tables.

In a typical experiment the results obtained were as follows : $CaBr_2,3n\text{-}C_3H_7{\cdot}OH - CaBr_2$ at 60°. P 766·7; p' 764·7; t 17·7°; f 15·0; d 0·99868; W 4281; M 60·06; m by loss in weight of saturator 0·2200; m by gain in weight of phosphorus pentoxide tube 0·2193; giving p by loss in weight of saturator 15·447, and by gain in weight of phosphorus pentoxide tube 15·398, in both cases in mm. of mercury.

The losses in weight of the saturators recorded in the present experiments were between 0·0148 and 0·6271 g., whilst the volumes of air employed fell between 356·4 and 14155 c.c.

In order to eliminate initial disturbances due to liquid alcohol adhering to the crystalline alcoholates each new charge in the saturator was aged by drawing through it a small volume of dry air before the readings were begun.

The present method is applicable only where the dissociation

pressure is lower than the vapour pressure of the pure alcohol at room temperature, since, if the former is greater than the latter, condensation will occur in the side tubes which emerge from the thermostat.

Results.

In Table I, $p_s^{t°}$ denotes the values of p at $t°$ determined from supersaturation, and $p_u^{t°}$ those determined from undersaturation, by the gain in weight of the P_2O_5 tube, and $p_l^{t°}$ and $p_g^{t°}$ denote the values of p determined from the loss in weight of the saturator and the gain in weight of the P_2O_5 tube, respectively.

TABLE I.

$CaBr_2,4CH_3{\cdot}OH$–$CaBr_2,3CH_3{\cdot}OH$.

$p_s^{20°}$ 19·99, 19·57, 19·78, 19·82, 19·88.
$p_u^{20°}$ 19·90, 19·90, 19·98, 19·94, 19·92.

$p_s^{30°}$ 40·70, 40·46, 40·58, 40·54, 40·60.
$p_u^{30°}$ 40·42, 40·28, 40·30, 40·28, 40·30.

$CaCl_2,4CH_3{\cdot}OH$–$CaCl_2,3CH_3{\cdot}OH$.

$p_l^{15°}$ 49·90, 49·70, 49·40, 49·60, 50·10, 49·84; mean 49·76.
$p_g^{15°}$ 48·90, 48·99, 48·92, 49·20, 49·09, 48·84; mean 48·84.

$p_l^{20°}$ 70·08, 70·14, 70·06, 70·15, 69·89, 70·00; mean 70·05.
$p_g^{20°}$ 69·80, 69·72, 69·69, 69·73, 69·73, 69·53; mean 69·70.

$p_l^{30°}$ 99·7, 100·5, 99·6, 99·2, 99·5, 99·8; mean 99·7.
$p_g^{30°}$ 98·8, 99·1, 98·6, 98·9, 99·0, 98·9; mean 98·9.

$CaBr_2,4CH_3{\cdot}OH$–$CaBr_2,3CH_3{\cdot}OH$.

$p_l^{15°}$ 13·55, 13·54, 13·62, 13·58, 13·72; mean 13·60.
$p_g^{15°}$ 13·52, 13·58, 13·59, 13·52, 13·60; mean 13·56.

$p_l^{20°}$ 19·91, 19·92, 19·96, 20·00, 19·93, 20·06; mean 19·96.
$p_g^{20°}$ 19·90, 19·90, 19·98, 19·94, 19·92, 20·02; mean 19·94.

$p_l^{30°}$ 40·45, 40·47, 40·30, 40·43, 40·28, 40·41, 40·36; mean 40·45.
$p_g^{30°}$ 40·42, 40·28, 40·30, 40·28, 40·30, 40·34; mean 40·32.

$p_l^{40°}$ 75·77, 75·80, 74·95, 75·87, 75·85, 75·54, 75·90; mean 75·67.
$p_g^{40°}$ 75·85, 75·50, 75·19, 75·58, 75·01, 75·49, 74·98; mean 75·37.

$CaCl_2,3C_2H_5{\cdot}OH$–$CaCl_2$.

$p_l^{30°}$ 7·81, 7·53, 8·00, 7·57, 7·72, 7·78; mean 7·74.
$p_l^{40°}$ 17·57, 17·67, 17·57, 17·83, 18·12, 18·28, 17·67, 17·79; mean 17·81.
$p_l^{50°}$ 48·56, 48·89, 48·58, 48·55, 49·40, 49·66, 49·20, 49·01; mean 48·98.

$CaBr_2,3C_2H_5{\cdot}OH$–$CaBr_2,C_2H_5{\cdot}OH$.

$p_l^{20°}$ 3·89, 3·70, 3·74, 3·92, 3·72, 3·83, 3·73, 3·77; mean 3·79.
$p_l^{30°}$ 9·45, 8·82, 9·06, 9·31, 9·49, 9·40, 9·25, 9·29; mean 9·32.
$p_l^{40°}$ 20·68, 20·18, 20·71, 20·76, 20·40, 20·76, 20·25, 20·95; mean 20·59.
$p_l^{50°}$ 41·48, 41·31, 41·65, 40·20, 41·81, 42·10, 42·00, 41·90; mean 41·55.
$p_l^{60°}$ 73·83, 72·88, 74·50, 73·04, 72·70, 73·40, 72·56, 73·02; mean 73·24.

TABLE I (*continued*).

$CaCl_2,3n\text{-}C_3H_7\cdot OH\text{–}CaCl_2$.

$p_l^{30°}$ 6·41, 6·50, 6·40, 6·44, 6·43, 6·46, 6·45, 6·42, 6·42, 6·45; mean 6·43.
$p_g^{30°}$ 6·40, 6·47, 6·40, 6·39, 6·38, 6·39, 6·42, 6·38, 6·40, 6·40; mean 6·40.

$p_l^{40°}$ 16·45, 16·32, 16·16, 16·38, 16·38, 16·28, 16·40, 16·37, 16·38, 16·43; mean 16·36.
$p_g^{40°}$ 16·27, 16·18, 16·14, 16·26, 16·31, 16·23, 16·32, 16·28, 16·20, 16·31; mean 16·25.

$p_l^{50°}$ 34·10, 34·12, 34·43, 34·30, 34·23, 34·11, 34·24, 34·14, 34·10, 34·37; mean 34·21.
$p_g^{50°}$ 34·02, 33·90, 34·34, 34·10, 34·01, 34·00, 34·08, 34·03, 34·03, 34·22; mean 34·17.

$CaBr_2,3n\text{-}C_3H_7\cdot OH\text{–}CaBr_2$.

$p_l^{30°}$ 1·70, 1·72, 1·73, 1·67, 1·71, 1·78, 1·70, 1·72, 1·72; mean 1·72.
$p_g^{30°}$ 1·70, 1·70, 1·67, 1·67, 1·67, 1·73, 1·69, 1·68, 1·71; mean 1·69.

$p_l^{40°}$ 3·73, 3·72, 3·77, 3·77, 3·76, 3·73, 3·76, 3·73, 3·72, 3·74; mean 3·74.
$p_g^{40°}$ 3·69, 3·66, 3·70, 3·67, 3·71, 3·66, 3·70, 3·66, 3·71, 3·68; mean 3·68.

$p_l^{50°}$ 7·61, 7·67, 7·65, 7·64, 7·66, 7·66, 7·69, 7·68, 7·67, 7·64; mean 7·66.
$p_g^{50°}$ 7·47, 7·55, 7·53, 7·55, 7·59, 7·57, 7·62, 7·58, 7·59, 7·55; mean 7·57.

$p_l^{60°}$ 15·59, 15·44, 15·63, 15·68, 15·54, 15·45, 15·63, 15·56, 15·50, 15·53; mean 15·56.
$p_g^{60°}$ 15·43, 15·18, 15·44, 15·50, 15·50, 15·40, 15·48, 15·42, 15·43, 15·48; mean 15·43.

$CaCl_2,3n\text{-}C_4H_9\cdot OH\text{–}CaCl_2$.

$p_l^{30°}$ 1·44, 1·42, 1·48, 1·49, 1·48, 1·46, 1·49, 1·47, 1·47, 1·47; mean 1·47.
$p_g^{30°}$ 1·44, 1·43, 1·47, 1·44, 1·43, 1·44, 1·47, 1·43, 1·43, 1·44; mean 1·44.

$p_l^{40°}$ 3·96, 3·64, 3·72, 3·66, 3·68, 3·70, 3·72, 3·75, 3·70, 3·70; mean 3·72.
$p_g^{40°}$ 3·94, 3·61, 3·68, 3·63, 3·64, 3·68, 3·69, 3·71, 3·70, 3·64; mean 3·69.

$p_l^{50°}$ 9·22, 9·18, 9·11, 9·10, 9·20, 9·16, 9·23, 9·15, 9·21, 9·21; mean 9·18.
$p_g^{50°}$ 9·08, 9·09, 9·10, 9·06, 9·13, 9·08, 9·21, 9·03, 9·08, 9·18; mean 9·09.

$p_l^{60°}$ 13·43, 13·52, 13·82, 13·50, 13·48, 13·55, 13·50, 13·49, 13·56, 13·42; mean 13·53.
$p_g^{60°}$ 13·26, 13·32, 13·61, 13·41, 13·39, 13·52, 13·31, 13·27, 13·40, 13·33; mean 13·38.

$CaBr_2,3n\text{-}C_4H_9\cdot OH\text{–}CaBr_2$.

$p_l^{30°}$ 1·56, 1·54, 1·59, 1·53, 1·59, 1·54, 1·60, 1·54, 1·56, 1·53; mean 1·56.
$p_g^{30°}$ 1·55, 1·52, 1·58, 1·53, 1·55, 1·53, 1·57, 1·54, 1·53, 1·52; mean 1·53.

$p_l^{40°}$ 2·84, 2·80, 2·81, 2·78, 2·85, 2·80, 2·81, 2·85, 2·83, 2·82; mean 2·82.
$p_g^{40°}$ 2·81, 2·81, 2·79, 2·77, 2·84, 2·79, 2·81, 2·84, 2·82, 2·80; mean 2·81.

$p_l^{50°}$ 5·08, 5·04, 5·07, 5·09, 5·05, 5·00, 5·08, 5·08, 4·99, 5·10; mean 5·06.
$p_g^{50°}$ 5·06, 5·01, 5·06, 5·08, 5·03, 5·00, 5·04, 5·04, 4·98, 5·05; mean 5·04.

$p_l^{60°}$ 9·38, 9·58, 9·36, 9·42, 9·48, 9·54, 9·57, 9·41, 9·45, 9·40; mean 9·46.
$p_g^{60°}$ 9·38, 9·48, 9·34, 9·36, 9·43, 9·49, 9·55, 9·41, 9·40, 9·35; mean 9·42.

Table II summarises the preceding results and gives the dissociation pressures in mm. of mercury at the various temperatures.

TABLE II.

Temp.	$CaCl_2$ 4—3 $CH_3{\cdot}OH$.	$CaBr_2$ 4—3 $CH_3{\cdot}OH$.	$CaCl_2$ 3—0 $C_2H_5{\cdot}OH$.	$CaBr_2$ 3—1 $C_2H_5{\cdot}OH$.	$CaCl_2$ 3—0 n-$C_3H_7{\cdot}OH$.	$CaBr_2$ 3—0 n-$C_3H_7{\cdot}OH$.	$CaCl_2$ 3—0 n-$C_4H_9{\cdot}OH$.	$CaBr_2$ 3—0 n-$C_4H_9{\cdot}OH$.
15°	49·30	13·58	—	—	—	—	—	—
20	69·88	19·95	—	3·79	—	—	—	—
30	99·3	40·39	7·74	9·32	6·42	1·71	1·45	1·55
40	—	75·52	17·81	20·59	16·31	3·71	3·70	2·82
50	—	—	48·98	41·55	34·19	7·62	9·14	5·05
60	—	—	—	73·24	—	15·50	13·45	9·44

Determinations of the dissociation pressures of other alcoholates are now in progress, and it is hoped to make the results obtained and the comparison of the affinities of the alcohols for salts the subjects of a further communication.

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XLIII.—*The* 4- *and* 4′-*Methoxybenzoylbenzoins.*

By HERBERT GREENE.

ALKALINE reagents and notably sodium ethoxide convert benzoylmandelonitrile (Francis and Davis, J., 1909, **95**, 1404) into benzoylbenzoin (Robinson and Robinson, P., 1913, **29**, 266; J., 1914, **105**, 1456). By adding benzaldehyde to the reaction mixture, Greene and Robinson (J., 1922, **121**, 2182) increased the yield of this product and found similarly that benzoylpiperoin was advantageously prepared from a mixture of benzoyl-3 : 4-methylenedioxymandelonitrile and piperonal. These observations were in harmony with Lapworth's view of the course of the benzoin reaction (J., 1903, **83**, 1004) and further evidence of a condensation of the aldol type was obtained when the interaction of benzoylmandelonitrile and anisaldehyde resulted in the isolation of a methoxybenzoylbenzoin melting at 119·5—120·5°. The structure of this product is discussed below.

It was also shown that 3 : 4-methylenedioxybenzoylbenzoin, $CH_2O_2{:}C_6H_3{\cdot}CO{\cdot}CH(OBz)Ph$ (I), is the main product of condensation between benzoyl-3 : 4-methylenedioxymandelonitrile and benzaldehyde, whereas 3′ : 4′-methylenedioxybenzoylbenzoin,

$$PhCO{\cdot}CH(OBz){\cdot}C_6H_3{:}O_2CH_2$$

(II), is obtained from benzoylmandelonitrile and piperonal. A migration of the benzoyl group was therefore definitely established.

By reducing the time of reaction, these products may be obtained almost pure, and the same is true of the piperonyl-furyl isomerides,

to which, by analogy, structures (III) and (IV) are assigned. The similarity existing between benzaldehyde and furfuraldehyde extends in this case to the yields of " mixed " benzoin. Thus substances (I) and (III) are obtained in small yield only (5 to 10%), whereas piperonal reacts with the benzoylcyanohydrins of these two aldehydes to give substances (II) and (IV) in much larger amount (25 to 30%).

$$CH_2O_2{:}C_6H_3{\cdot}CH(OBz){\cdot}CN + CHO{\cdot}C_4H_3O \longrightarrow CH_2O_2{:}C_6H_3{\cdot}CO{\cdot}CH(OBz){\cdot}C_4H_3O \quad \text{(III.)}$$

$$\text{(VII.)}\quad C_4H_3O{\cdot}CH(OBz){\cdot}CN + CH_2O_2{:}C_6H_3{\cdot}CHO \longrightarrow C_4H_3O{\cdot}CO{\cdot}CH(OBz){\cdot}C_6H_3{:}O_2CH_2 \quad \text{(IV.)}$$

In the same way, anisaldehyde and benzoylmandelonitrile react to give 4′-methoxybenzoylbenzoin (V; m. p. 127—128°), whilst benzoyl-*p*-methoxymandelonitrile and benzaldehyde yield the isomeric 4-methoxybenzoylbenzoin (VI; m. p. 119·5—120·5°). Here, however, the allocation of formulæ is not so simple, for the lower-melting isomeride is also obtainable from the other reaction mixture (Greene and Robinson,* *loc. cit.*, p. 2189). In fact, either of the isomerides may be obtained from benzoylmandelonitrile and anisaldehyde. The reaction system is very sensitive to changes in the experimental conditions, which have therefore been studied in detail.

On standing in contact with cold sodium ethoxide solution, both isomerides are hydrolysed to *p*-methoxybenzoin (Ekecrantz and Ahlqvist, *Arkiv Kem. Min. Geol.*, 1908, **3**, No. 13, 26). It is desirable, therefore, to interrupt the reactions some 15 minutes after addition of the condensing agent, and when this is done the yields are roughly as follows :

	Benzoylmandelonitrile and anisaldehyde.	Benzoyl-*p*-methoxymandelonitrile and benzaldehyde.
½ Mol. of NaOEt. Rapid interruption.	Higher-melting isomeride, 30%.	No crystalline product.
1 Mol. of NaOEt. Rapid interruption.	Lower-melting isomeride, 8%.	Lower-melting isomeride, 15%.
½ Mol. of NaOEt. Gradual addition.	Both isomerides.	Benzoylbenzoin.

In the cases mentioned above, the diminution of the quantity of sodium ethoxide to a half-molecular proportion leads to the spontaneous separation of substances I, II, III, and IV. It seems reasonable, therefore, to regard the isomeride melting at 127—128° as the normal product of condensation between benzoylmandelonitrile and anisaldehyde, and this substance is therefore 4′-methoxybenzoylbenzoin. The isomeride of m. p. 119·5—120·5° is accord-

* Compare this communication for the scheme of numbering.

ingly 4-methoxybenzoylbenzoin and its occurrence as a product of condensation of benzoylmandelonitrile and anisaldehyde appears to be due to a double decomposition which results in the formation of benzaldehyde and benzoyl-*p*-methoxymandelonitrile. The following results demonstrate that such a reaction can occur. Attempted condensations of benzoylmandelonitrile and furfuraldehyde on the one hand and of benzoylfurfuraldehydecyanohydrin (VII) and benzaldehyde on the other have uniformly furnished mixtures of benzoylbenzoin (m. p. 125°) and benzoylfuroin (m. p. 92—93°) in slightly varying proportions.

It is clear that the formation of benzoylfuroin from benzoylmandelonitrile and furfuraldehyde involves preliminary transference of the benzoyl cyanide addenda from benzaldehyde to furfuraldehyde. The benzoylfurfuraldehydecyanohydrin so formed then reacts with unchanged furfuraldehyde in the normal manner, and benzoylfurion is, in fact, readily accessible through this derivative. In the second series of experiments, we have the inverse change. Some benzoylmandelonitrile is formed at the expense of the benzoylfurfuraldehydecyanohydrin, and it then reacts with unchanged benzaldehyde, yielding benzoylbenzoin. All these reaction mixtures originally contained excess of free aldehyde, and accordingly, where the gradual addition of sodium ethoxide during a period of three or four hours has favoured equilibrium, the products of this type of change are present in relatively greater amount.

Under similar conditions, benzoylbenzoin was actually the only crystalline product obtained from benzoyl-*p*-methoxymandelonitrile and benzaldehyde (table above). Here again we must infer degradation of the original nitrile and formation of benzoylmandelonitrile, which subsequently undergoes its normal condensation with unchanged benzaldehyde. With benzoylmandelonitrile and anisaldehyde, the concomitant processes are represented by the scheme below, in which it has not been considered necessary to illustrate the contemporaneous formation of benzoylbenzoin and benzoylanisoin.

$$MeO{\cdot}C_6H_4{\cdot}CHO + Ph{\cdot}CH(OBz){\cdot}CN \longrightarrow \underset{(V.)}{MeO{\cdot}C_6H_4{\cdot}CH(OBz){\cdot}COPh}$$

$$MeO{\cdot}C_6H_4{\cdot}CH(OBz){\cdot}CN + Ph{\cdot}CHO \longrightarrow \underset{(VI.)}{MeO{\cdot}C_6H_4{\cdot}CO{\cdot}CH(OBz)Ph}$$

In the studies now recorded, the formation of isomeric derivatives of mixed benzoins was observed in three out of four cases. It is apparently favoured by disparity of the constituent aldehydes.

EXPERIMENTAL.

Benzoylfurfuraldehydecyanohydrin.—Always a good and, on one occasion, a practically theoretical yield of this substance was

obtained by application of the general method of Francis and Davis (*loc. cit.*). Furfuraldehyde (24 g.), benzoyl chloride (35 g.), and a solution of potassium cyanide (17 g.) in water (200 c.c.) were shaken together for 1 hour with cooling. The product separated from 90% alcohol in colourless, hexagonal plates (Found : C, 68·9; H, 4·3. $C_{13}H_9O_3N$ requires C, 68·7; H, 4·0%). This material, m. p. 48°, was used for the preparation of the derivatives described below. Distillation under reduced pressure and recrystallisation from alcohol raise the melting point to 49°.

Benzoylfuroin, $C_4H_3O{\cdot}CO{\cdot}CH(OBz){\cdot}C_4H_3O$.—A cold solution of sodium ethoxide (0·6 g. of sodium) in ethyl alcohol (30 c.c.) was rapidly added to one of benzoylfurfuraldehydecyanohydrin (11 g.) and furfuraldehyde (12 g.) in ethyl alcohol (25 c.c.). The reaction mixture was shaken for 4 minutes in running water, which checked a slight rise of temperature, and then cooled in ice-water. The product that separated was collected after 15 minutes and extracted with boiling ethyl alcohol (20 c.c.). The filtered solution yielded 6·15 g., m. p. 92—93° (Found for twice recrystallised material : C, 68·7; H, 4·1. $C_{17}H_{12}O_5$ requires C, 68·9; H, 4·0%); a further 1·2 g., m. p. 91—93°, could be isolated. The substance separates from alcohol in colourless octahedra, the predominant prismatic modification being derived by prolongation along one axis. With cold concentrated sulphuric acid, an intense green colour is developed and this gradually changes to brown on warming. By the action of alcoholic sodium ethoxide, a small amount of furil, m. p. 164°, was produced, which was identified by the melting point of its mixture with an authentic sample (E. Fischer, *Annalen*, 1882, **211**, 221).

Benzfuroin.—It seemed possible to clear up the question as to whether benzfuroin (E. Fischer, *loc. cit.*) is a single substance by benzoylating it and comparing the product with the isomeric benzoylbenzfuroins.

Benzfuroin was recovered unchanged after being shaken with aqueous potassium hydroxide and benzoyl chloride, even in presence of ether, or with pyridine and benzoyl chloride, and heating with the acid chloride alone resulted in profound decomposition. Difficulties of quite another kind were met in attempts, described in detail below, to prepare the isomeric derivatives; for the most part, mixtures of benzoylbenzoin and benzoylfuroin were obtained. Neither of the required isomerides being present in isolable amount, this method of attack was abandoned. There are, however, grounds for believing that benzfuroin is a mixture of two isomerides.

The melting points of four preparations of benzfuroin showed variations (recorded : 135—141°, 134—135°, 134—137°, 138—140°).

These may, of course, be due in part to the presence of benzoin or furoin. Benzfuroin was the sole product isolated in an attempt to prepare a benzoylbenzfuroin by the very slow addition, during 5 or 6 hours with water cooling, of sodium ethoxide (1·15 g. of sodium) in ethyl alcohol (40 c.c.) to a cold solution of benzoylmandelonitrile (11 g.) and furfuraldehyde (12 g.) in ethyl alcohol (40 c.c.). The product (1·9 g.) was isolated by means of ether and crystallised from boiling water, giving 0·5 g. of long, feathery crystals, m. p. 139—141°. The granular, amorphous residue was recrystallised from a little absolute alcohol and then from aqueous alcohol. This material (0·2 g.) melted at 141·5—143·5°, and at 138—140° when mixed with the other fraction or with benzfuroin (m. p. 137—139°) prepared by Fischer's method. The possibility that benzfuroin was here the product of hydrolysis again suggests its composite character. Finally, apart from decomposition, the material was practically unchanged by the action of boiling alcoholic sodium ethoxide, a reagent which doubtless induces enolisation. The recovered material softened at 136° and melted at 140—142°, alone or mixed with the original material.

Attempts to prepare Isomeric Benzoylbenzfuroins.—In each experiment the reaction mixture was treated with ether and water. The ethereal layer was washed successively with aqueous sodium bisulphite, sodium carbonate solution, and water, and dried with anhydrous sodium sulphate. The following table summarises the results of the experiments.

	Products from	
	Benzoylmandelonitrile and furfuraldehyde.	Benzoylfurfuraldehydecyanohydrin and benzaldehyde.
½ Mol. of NaOEt. Rapid interruption.	Benzoylbenzoin and benzoylfuroin.	Benzoylbenzoin and benzoylfuroin.
1 Mol. of NaOEt. Rapid interruption.	Ditto (together with benzfuroin).	Benzoylbenzoin and benzoylfuroin (A).
½ Mol. of NaOEt. Gradual addition.	Ditto (richer in benzoylfuroin).	Ditto (richer in benzoylbenzoin).

The following is a typical experiment resulting in the formation of the product (A). A solution of sodium ethoxide (1·15 g. of sodium) in ethyl alcohol (30 c.c.) was added in one portion to one of benzoylfurfuraldehydecyanohydrin (11·4 g.) and benzaldehyde (10 g.) in ethyl alcohol (30 c.c.). The mixture was shaken in running water for 15 minutes and then extracted as above. After removal of solvent and addition of a little methyl alcohol, crystals readily separated, which were filtered off after 3 hours (4·3 g.). Recrystallised from 90% alcohol (15 c.c.), they melted at 87—88° and showed under the microscope a variety of shapes strongly resembling those observed in the case of 4-methoxybenzoylbenzoin. This crop was

recrystallised from 90% alcohol (15 c.c.), giving two crops, and a third by addition of water : Crop I, 2·45 g., m. p. 86—87°; crop II, 0·75 g., m. p. 87°; crop III, 0·26 g., m. p. 85—87°. Crop I, recrystallised from absolute alcohol, gave two crops, of which the larger weighed 2·19 g. and melted at 86—87°. It still showed a variety of shapes under the microscope (Found : C, 74·0; H, 4·7. $C_{21}H_{16}O_3 + C_{17}H_{12}O_5$ requires C, 74·5; H, 4·6%). For comparative purposes, an equimolecular mixture of benzoylfuroin and benzoylbenzoin was prepared. After preliminary softening, this began to melt at 85·5° and still contained some solid at 90°, whilst when mixed with product (A) it melted at 84·5—88°. This leads us to conclude that both mixtures are in the neighbourhood of the eutectic. Product (A) is therefore a mixture containing benzoylfuroin, benzoylbenzoin, and probably some benzoylbenzfuroin, although this has on no occasion been isolated.

4-*Methoxybenzoylbenzoin* (VI; m. p. 119·5—120·5°).—This substance, obtained with fortuitous ease from a reaction mixture of benzoylmandelonitrile and anisaldehyde, was described (Greene and Robinson, *loc. cit.*) as 4′-methoxybenzoylbenzoin. Reasons for adopting the alternative configuration have now been given.

4-Methoxybenzoylbenzoin is best prepared by condensing benzoyl-*p*-methoxymandelonitrile and benzaldehyde. The reaction requires rather more than 1 mol. of sodium ethoxide and should be rapidly interrupted. Thus 1·5 g. of nearly pure material were obtained when a solution of sodium ethoxide (0·6 g. of sodium) in alcohol (20 c.c.) was added in one portion to the nitrile (7·3 g.) and benzaldehyde (10 g.) in cold alcoholic solution (20 c.c.). The reaction lasted 10 minutes.

To observe the abnormal production of this isomeride from benzoylmandelonitrile and anisaldehyde, it is desirable to reduce the time of reaction and so check hydrolysis. A solution of sodium ethoxide (1·3 g. of sodium) in alcohol (25 c.c.) was added in one lot to a solution of benzoylmandelonitrile (12 g.) and anisaldehyde (11 g.) in alcohol (30 c.c.). Rise of temperature was checked by shaking the reaction mixture in running water, and after 7 minutes the material was extracted by addition of ether and water. After removal of the solvent, the residual liquor was treated with methyl alcohol and light petroleum. Cooling in ice and salt gave crystals which, once recrystallised from alcohol, weighed 0·9 g. and melted between 118° and 120°. These were identical with the original specimen (Greene and Robinson, *loc. cit.*) (Found : MeO, 7·9, 8·1. Calc. for $C_{22}H_{18}O_4$, MeO, 9·0%).

Abnormal Production of Benzoylbenzoin.—On three occasions when ½ mol. of sodium ethoxide was added drop by drop to alcoholic

solutions of benzoyl-*p*-methoxymandelonitrile and benzaldehyde, small quantities of benzoylbenzoin were obtained in a good state of purity. This unexpected result was ascertained in one case by combustion and the method of mixed melting point and in the others by the latter method only. The characteristic prismatic rods of benzoylbenzoin were also readily recognisable under the microscope. The yields of this product, starting in each case from 11·5 g. of benzoyl-*p*-methoxymandelonitrile and 11 g. of benzaldehyde, were 1·6 g. (m. p. 122—125°), 0·7 g. (m. p. 120—123°), and 0·6 g. (m. p. 119—122°), respectively. The condensation of benzoyl-*p*-methoxymandelonitrile with anisaldehyde does not afford a convenient means of preparing benzoylanisoin.

4′-*Methoxybenzoylbenzoin* (V; m. p. 127—128°).—A solution of sodium ethoxide (1·15 g. of sodium) in ethyl alcohol (30 c.c.) was added in one portion to benzoylmandelonitrile (23 g.) and anisaldehyde (22·5 g.) dissolved in ethyl alcohol (30 c.c.). The mixture was shaken in running water for 5 minutes and then worked up in the usual manner. The crystals (3·4 g.) which separated from the ether, recrystallised from 90% alcohol (75 c.c.), had m. p. 125—127°. The ethereal mother-liquor was treated as usual, and the crop recovered from the drying agent (magnesium sulphate) by addition of water, on recrystallisation, gave 4·9 g. of m. p. 124—127°; from the ethereal solution 2·4 g. of m. p. 121—124° were obtained. The pure product melted at 127—128° (Found : C, 76·1; H, 5·3; MeO, 8·5. $C_{22}H_{18}O_4$ requires C, 76·3; H, 5·2; MeO, 9·0%). A mixture with the isomeride described above melted at 100—104°. 4′-Methoxybenzoylbenzoin crystallises from alcohol or ether in colourless, prismatic rods and dissolves in cold concentrated sulphuric acid to a brassy yellow solution which, on warming, remains yellow for a time and then suddenly passes through reddish-brown to dark greenish-brown.

A further illustration of the sensitive nature of the general reaction was provided by an experiment in which a cold solution of sodium ethoxide (0·6 g. of sodium) in alcohol (25 c.c.) was, during 3 or 4 hours, gradually added to a cold solution of benzoylmandelonitrile (12 g.) and anisaldehyde (11 g.) in ethyl alcohol (30 c.c.). Some crystals separated during the course of the reaction, which was controlled by water cooling. These were filtered off, washed with water and alcohol, and recrystallised from alcohol. The substance (0·1 g.) had m. p. 120—124°, which was raised to 120—126° by admixture with 4′-methoxybenzoylbenzoin and depressed by admixture with the other isomeride. The filtrate of the reaction mixture was extracted as usual and gave a syrup from which, by nucleation, 4-methoxybenzoylbenzoin (0·3 g.) was obtained.

Piperonoyl-α-furylcarbinyl Benzoate (III).—This substance was obtained from benzoylmethylenedioxymandelonitrile (28 g.) and furfuraldehyde (23 g.) in alcohol (30 c.c.) by addition in one lot of a solution of sodium ethoxide (1·15 g. of sodium) in ethyl alcohol (30 c.c.). The mixture was shaken in running water for 5 minutes and then extracted as in other cases. From the ethereal solution, a crop was obtained which, after one recrystallisation from 90% alcohol (45 c.c.), gave 3·3 g. of crystals, m. p. 130—132°. A smaller fraction (1·3 g.), m. p. 117—130°, was recovered from the drying agent. In two half-scale experiments the yields were 1·4 g. of m. p. 125—130° and 1·6 g. of m. p. 125—129°. In the former, the reaction was allowed to proceed for 20 minutes before extraction, and this delay seems to have decreased the yield. Increase of the proportion of sodium to 1·1 g. for 14·1 g. of nitrile in a reaction which lasted 15 minutes led to the isolation of an impure product (3·4 g.), m. p. 103—106°.

From the three earlier experiments were obtained 6·6 g. of material, m. p. 131·5—133·5°, and for analysis a portion of this was recrystallised from glacial acetic acid, toluene and rectified spirit. The pure product melted at 132·5—133·5° (Found : C, 68·5; H, 4·1. $C_{20}H_{14}O_6$ requires C, 68·6; H, 4·0%). The substance crystallised from alcohol in colourless, prismatic rods and when mixed with its isomeride of m. p. 140—141°, melted at 110—115°.

α-Furoylpiperonylcarbinyl Benzoate (IV).—This substance was prepared readily and in good yield by the condensation of piperonal (12 g.) with benzoylfurfuraldehydecyanohydrin (11 g.) in ethyl alcohol (40 c.c.). Sodium ethoxide (0·6 g. of sodium) in ethyl alcohol (20 c.c.) was added in one portion and the mixture was shaken in running water. After 25 minutes, the solid was collected, and only a minute quantity was recovered from the mother-liquor. The substance was recrystallised from glacial acetic acid (25 c.c.) and from ethyl alcohol (80 c.c.), and the main crop (4·7 g.) had m. p. 136—138°. For analysis, this material was recrystallised from alcohol, glacial acetic acid, 90% alcohol, toluene, and 90% alcohol, giving 3·1 g. of the pure substance, m. p. 140—141° (Found : C, 68·8; H, 4·1. $C_{20}H_{14}O_6$ requires C, 68·6; H, 4·0%). The colourless, hexagonal plates dissolve in cold concentrated sulphuric acid to an intense crimson solution tinged with brown.

3 : 4- and 3′ : 4′-*Methylenedioxybenzoylbenzoins* (I and II).—By reducing the time of reaction hydrolysis has been lessened and more convenient methods of preparing these isomerides are now submitted.

A solution of sodium ethoxide (0·6 g. of sodium) in ethyl alcohol (20 c.c.) was added to benzoylmandelonitrile (12 g.) and piperonal (11 g.) in ethyl alcohol (40 c.c.). The mixture was shaken in

running water for 15 minutes and extracted with ether. The solid residue was crystallised from glacial acetic acid, giving 2·6 g. of material, m. p. 132·5—134·5°, and 1·1 g., m. p. 129—132°. The ethereal solution after the usual treatment gave 1·9 g. of crystals, m. p. 127—131°. A portion of this product, recrystallised once, was identical with authentic 3′ : 4′-methylenedioxybenzoylbenzoin, m. p. 134—135°.

From benzoylmethylenedioxymandelonitrile (14·1 g.) and benzaldehyde (11 g.) dissolved in alcohol (40 c.c.) there were obtained, by addition, in one portion, of a solution of sodium ethoxide (0·6 g. of sodium) in alcohol (20 c.c.), 1·1 g. of a product, m. p. 144—147°, and 146—148° when mixed with 3 : 4-methylenedioxybenzoylbenzoin (m. p. 147·5—148·5°). In this experiment, the reaction was allowed to continue for 35 minutes.

When the time of reaction and the quantities of nitrile and aldehyde (but not of sodium) were halved, the percentage yield was almost doubled.

This work was carried out at the Universities of St. Andrews and Manchester. The author takes this opportunity of thanking Prof. R. Robinson, F.R.S., for his interest in it, and also the Carnegie Trustees for the award of a scholarship.

WELLCOME TROPICAL RESEARCH LABORATORIES,
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XLIV.—*The Reaction between Hydroxylamine and Ferric Chloride.*

By ALEC DUNCAN MITCHELL.

HYDROXYLAMINE is a compound of great interest from several points of view. Many years ago Haber showed (*Ber.*, 1896, **29**, 2444) that it would oxidise ferrous salts in alkaline solution or suspension, and reduce ferric salts in acid solution, and he suggested that its structure in the two cases might be represented as $H_3N{:}O$ and $H_2N{\cdot}OH$ respectively. The existence of such dynamic isomerides would account for the above behaviour, which is typical of many of the reactions of hydroxylamine, and, with the object of seeking a further basis for this hypothesis, the author has carried out several kinetic studies, since similar investigations have afforded such evidence in other cases (Mitchell, J., 1923, **123**, 629, 2241).

The reactions of hydroxylamine are all very complicated, and, up to the present, only one, the subject of this communication, has been interpreted. It may be stated at once that, possibly because

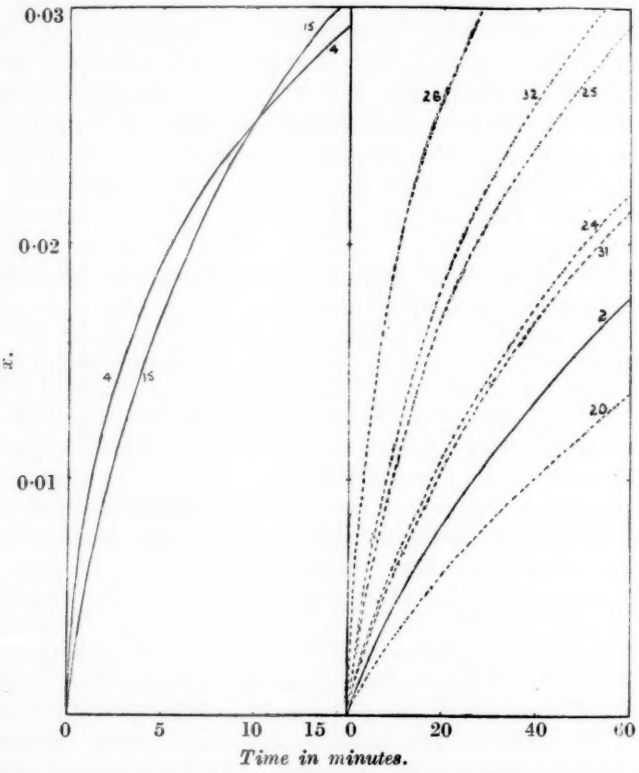
the acidic solutions involved may exclude one isomeride, the results have no bearing on the main problem, but they are of interest in other respects.

A kinetic study of the reactions of hydroxylamine appeared desirable in that no such examination has hitherto been made. A survey of the literature discloses more than twenty reactions in which the ultimate products have been studied, but the mechanism underlying their formation has usually been ignored. There are two partial exceptions to this statement: (1) Raschig ("Schwefel- und Stickstoff-Studien," 1924) studied the stoicheiometrical ratios obtaining at various stages in the course of certain reactions, but did not investigate them kinetically; and (2) Brönsted (*Z. physikal. Chem.*, 1922, **102**, 187) made a rough colorimetric estimate of the effect of a saline solution on the reaction now discussed, and, from the apparent absence of appreciable "salt effect," concluded that reaction takes place between the metallic ion and undissociated hydroxylamine molecule to form a "critical complex." As will be seen later, however, the more accurate method used here indicates a definite negative salt effect (p. 347).

There seemed to be two difficulties in the way of the proposed investigations: (1) few of the reactions proceed quantitatively in one direction, the majority giving varying proportions of by-products, and (2) hydroxylamine reacts more or less readily with most of the reagents which might normally be employed in the estimation of the second reactant or the products. The second difficulty has been obviated in the present instance by analytical methods which are described in the experimental portion of this communication. The first difficulty has been minimised by choosing reactions, such as that under discussion, which appear to give but little by-product. In the present case, the reaction is quantitative under the conditions laid down by Raschig (*Annalen*, 1887, **241**, 190)—considerable excess of ferric salt and of sulphuric acid, and at least five minutes' boiling. These conditions could not, for various reasons, be applied in the present research, but it is believed that the necessary departures from them involve only slight errors. There is no doubt that the difficulties which had to be overcome by Raschig were the slowness of the reaction in its later stages and the possible persistence of an intermediate product. The former difficulty is immaterial in an investigation such as this, and the latter is only of importance in so far as it affects analysis, but the method used is believed to eliminate this effect (p. 346). A consideration of the work of Bray (*J. Amer. Chem. Soc.*, 1919, **41**, 1363) in conjunction with that of Kurtenacker and Neusser (*Z. anorg. Chem.*, 1923, **131**, 27) shows that, using only a bare excess of ferric salt, reaction is incomplete

simply because it becomes extremely slow, and that, using neutral or very feebly acidic solutions, there is slight formation of elementary nitrogen, corresponding to 4%, at most, of the hydroxylamine. Apart from this, these authors find no evidence of side-reactions, and it would therefore appear that the departures from the prescribed conditions do not materially affect the present research. The author's experience confirms the production of traces of nitrogen

FIG. 1.



in the least acidic solutions, and also indicates that, under the conditions which are imposed upon this research—restrictions which often necessarily obtain in kinetic studies—traces of higher oxides of nitrogen are produced (p. 346).

Mechanism of the Reaction.

The complete reaction under ideal conditions is represented by

$$4Fe''' + 2NH_3OH^{\cdot} = 4Fe'' + 6H^{\cdot} + N_2O + H_2O$$

and the molar concentrations of the first four species will be repre-

sented by a, $b/2$, f, and h respectively. It will be seen that, if the suffix 0 represent these at zero-time, and the suffix t at any specified time corresponding to the reduction of x moles of ferric iron, then $a_t = a_0 - x$, $b_t = b_o - x$, $f_t = f_0 + x$, and $h_t = h_0 + 3x/2$.

A few experiments using ferric chloride and hydroxylamine hydrochloride led to no conclusion as to the order of the reaction. The initial velocity was enormous, but was damped down so rapidly that, unless a reaction of about the tenth order was assumed, one had to ascribe repressing effects to one or more of the products of reaction. Even when the velocity became of a lower order, a reduction of, say, 5%, in the concentrations of ferric iron and hydroxylamine caused the velocity to be reduced to one-half or less (see Expt. 1 as an example). (The reduction of cupric salts by hydroxylamine in the presence of acetic acid and sodium acetate is found to be similar in this respect.)

The initial addition of hydrochloric acid produced much slower reactions, but the damping was still so marked that a second product of reaction was suspected of a repressing effect (see Fig. 1, Expt. 4). Initial addition of ferrous salts also produced a great depression in velocity whether hydrochloric acid had been added or not. (The effects of equi-molar additions of hydrochloric acid or ferrous salts were not quite the same.) When both hydrochloric acid and ferrous salts were present in fair concentration, the reaction was closely termolecular—bimolecular with regard to ferric iron and unimolecular with respect to hydroxylamine. The termolecular velocity coefficient fell off slightly, but this was provisionally attributed to the progressive accumulation of ferrous and hydrogen ions, as reaction in the presence of a large excess of both was too slow for a more rigid test to be practicable. No other type of ordinary velocity coefficient gave any approach to constancy.*

* In this connexion may be mentioned an interesting instance of the danger of relying on initial velocities from a few isolated experiments as a clue to the order of reaction: in a few runs with initial hydrochloric acid and hydroxylamine kept constant, the apparent initial velocity (that based on the gross change before the first titration) was roughly proportional to the initial concentration of ferric chloride, which was varied, and the erroneous deduction was drawn that this was involved to only the first order. The explanation is due to the fact that, as will be seen later, the velocity in these experiments is inversely proportional to the concentration of ferrous iron, so that $\delta x \propto a^2/f$; since f increases from zero to δx in the small interval concerned, its mean concentration is $\delta x/2$, so that $\delta x \propto a^2/\delta x/2$ as an approximation, or $(\delta x)^2 \propto a^2$ or $\delta x \propto a$—thus accounting for the erroneous conclusion. Strictly, one is dealing with an integral summation starting with an infinite velocity for an infinitely short time, but actually the velocity is of a measurable order almost instantly, so that the approximation involved here is sufficiently near the truth to account for the observed facts.

The effects of the products of the reaction in repressing it indicated an equilibrium as an *intermediate* stage in the reaction; and it could be *only an intermediate stage* because the reaction goes to completion, forming the basis of Raschig's method for the estimation of hydroxylamine, so that the ultimate products could not reverse the reaction.

Further evidence bearing on the equilibrium was obtained when certain experiments, the early stages of which were too rapid for detailed measurement at 25°, were carried out at 15·5°. Seven experiments, of various types, all gave the temperature coefficient of 5·9 for 9·5°, which, by exponential proportion, becomes 6·5 for 10°. Just as temperature coefficients of less than unity—or negative coefficients as they would be if expressed more rationally—are interpreted as evidence of intermediate compounds (Eggert, *Z. Elektrochem.*, 1921, **27**, 455, and Skrabal, *ibid.*, 1915, **21**, 461, on the Landolt reaction, and Hasche and Patrick, *J. Amer. Chem. Soc.*, 1925, **47**, 1214, on the reaction between nitric oxide and oxygen), so this abnormally high temperature coefficient is regarded as indicating the existence of an intermediate equilibrium, which is displaced, by a rise in temperature, in a direction more favourable to reaction, this accelerating effect being superimposed upon the normal temperature effect.

No attempt has been made to correct for incomplete ionisation of electrolytes; the corrections which have been made for salt effect (p. 349) in certain cases tend to make a rough correction of this kind, however, and serve to make experiments more comparable.

The recognised methods of treating reaction velocities fail where the indications are that the initial velocity is infinite or of a very high magnitude. It was therefore necessary to obtain expressions, even if they were empirical, which would represent the course of the reaction, before one could draw any conclusions of a quantitative nature, and subsequently a certain amount of theoretical justification was found for them. As a tentative expression the following was used:

$$\frac{dx}{dt} = k_1 \frac{(a-x)^2(b-x)}{(h+3x/2)(f+x)} \quad . \quad . \quad . \quad . \quad . \quad (1)^*$$

It is here necessary for the purposes of discussion to classify experiments into four types as follows:

(I) Those having only ferric chloride and hydroxylamine hydrochloride initially.

(II) Those having additional hydrochloric acid alone initially.

(III) Those having additional ferrous iron alone initially.

* The integrals of all the formulæ used here are very cumbersome and their calculations are tedious, so details are omitted.

(IV). Those having both additional hydrochloric acid and ferrous iron initially.

Expression (1) gave for all experiments, except those of type (I), values for k_1 which were reasonably constant in any one experiment, as is shown for two types by Expts. 5 and 18. The values showed a slight tendency to fall as a rule, and, as will be seen in the table, varied from one experiment to another in such a way as to suggest that the second power of $(h + 3x/2)$ should replace the first power. When this amended expression

$$\frac{dx}{dt} = k_2 \frac{(a - x)^2(b - x)}{(h + 3x/2)^2(f + x)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

is applied to the experiments the results are as shown in the same table. In this table, the values of a, b, f, and h are expressed in moles per litre and relate to initial conditions; the values of k_1 and k_2 as found from the differential determinations of velocity (see p. 347) are shown as well as those obtained by integration: the latter often obscure marked drifts towards the end of a reaction and thus are not so trustworthy in these circumstances as the differential values, although they are far less subject to experimental error. In experiments of types (I), (II), and (III), where the initial velocity is very great, the integrated values are a more trustworthy guide as to the course of the early stages of the reaction. Although k_2 shows a rise throughout every reaction, it is noteworthy that its order of magnitude is very consistent throughout the whole range of experiments, which cover a wide variety of conditions and are usually continued until over 50% of the possible reaction is completed—this extent is indicated for each experiment in the column "% completed." As it was highly improbable that this consistency was a mere coincidence, a search was made for a theoretical basis which would account for the general agreement and possibly afford a reason for the anomalies noticed.

If the hypothetical nitroxyl were produced according to the equation $2Fe^{\cdot\cdot\cdot}+NH_3OH^{\cdot} \rightleftharpoons 2Fe^{\cdot\cdot}+3H^{\cdot}+HNO$ (and subsequently decomposed to nitrous oxide), this would be expected to play a part in the repression of the reaction, and the effect of ferrous and hydrogen ions would be more nearly in proportion to the second and third powers of their respective concentrations. As a matter of fact, the introduction into the formulæ of any function of x, giving, for example, $dx/dt = ka^2b/hfx$ or $dx/dt = ka^2b/h^2fx$, renders them quite incapable of representing the course of reaction; and the use of the second or third powers of f or h respectively is similarly useless. The absence from (2) of any term representing an intermediate compound seems to be capable of explanation as follows.

One has circumstantial evidence for assuming the formation of a complex, thus:

$$2Fe^{\cdots} + NH_3OH^{\cdot} \rightleftharpoons Fe^{\cdot\cdot} + 2H^{\cdot} + (Fe,H,NOH)^{\cdots};$$

denoting the complex by M and its concentration by m, and assuming it to decompose to nitrous oxide according to a unimolecular law, we have for the rate of accumulation of M:

$$dm/dt = k_3a^2b - k_4h^2fm - k_5m \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and for the rate of diminution of ferric iron:

$$dx/dt = k_3a^2b - k_4h^2fm = dm/dt + k_5m \quad . \quad . \quad . \quad . \quad (4)$$

(If one deals with the very early stages of reaction, it would be necessary to allow for the fact that a certain amount of hydrogen and ferrous ions is locked up in the complex M, and is therefore present as such in a concentration less by an amount m than the values $(h + 3x/2)$ and $(f + x)$; the error involved by ignoring this is small when h_0 and f_0 are finite, however, and the equations would become extremely complicated.)

After the very early stages of a reaction, m tends to keep nearly constant, owing to a compensating effect of the three reactions tending to adjust it; one would then have $dm/dt = 0$, and $dx/dt = k_5m = k_3a^2b - k_4h^2fm$. Solving for m and substituting, one has

$$dx/dt = k_3k_5a^2b/(k_4h^2f + k_5) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

When both h_0 and f_0 are zero, $dx/dt = k_3a^2b$, independently of any simplifying assumptions, and, since reaction is so rapid, it is certain that k_3 must be very large. Such a condition only obtains in the initial stages, to which expression (5) does not apply, owing to the nature of the assumptions made. The term k_4h^2f in experiments of types (II) and (III) rapidly becomes of a finite order, and in type (IV) is already of a finite order, so that, as soon as k_4h^2f becomes markedly greater than k_5, one arrives at the same expression as was obtained empirically, k_3k_5/k_4 being equal to k_2 in (2). The expressions (3) and (4) are too complicated for complete solution, so that one is unable to find whether they would account for the rise in the value of k_2 or for certain other discrepancies to be discussed later.

It is possible that reaction involves the free undissociated basic molecule: $2Fe^{\cdots} + NH_2{\cdot}OH \rightleftharpoons Fe^{\cdot\cdot} + H^{\cdot} + (NOH, Fe,H)^{\cdots}$. This mechanism would lead to an expression such as (1) but the term $(b - x)$ would have to be corrected in order to make it correspond to the free base. After the hydrogen-ion concentration reaches a value which is very early attained in experiments of types (I) and (III) and which obtains initially in the other types, this corrected

term becomes approximately $(b - x)k_h/(h + 3x/2)$, k_h being the hydrolytic dissociation constant of hydroxylamine hydrochloride. An expression similar to (2) therefore results, and, as this expression is not applicable to the early stages, a decision between this possibility and that developed above cannot be made. It is believed, however, that the extremely rapid fall in the initial concentration of free basic molecules in experiments of types (I) and (III) would require an even greater fall in velocity than is actually found, so that the foregoing hypothesis is preferred.

Discussion of Results.

An apparent anomaly is exhibited by Expts. 15 and 23 in type (III), since k_1 rises at first in these cases but falls as a rule, and in this type alone k_2 appears to be zero initially. The latter fact is immaterial in view of the way in which k_2 is derived on theoretical grounds, and it cannot be expected to hold at $t = 0$. The fact that k_1 exhibited a different behaviour in these experiments from the more usual behaviour is connected with the circumstance that initial ferrous iron depresses more than initial equi-molar hydrogen ions, as is shown by the curves for Expts. 4 and 15 (Fig. 1), Expts. 22 and 23 being similar. In each case, however, as the curves show, the experiment with more ferrous iron overtakes the other as hydrogen ions accumulate during the progress of the reaction, and then one has the conditions which prevail in type (IV), where hydrogen ions depress to a greater extent than the equi-molar ferrous ions —see Expts. 17 and 18 or 13 and 14. All these peculiarities become normal when one considers the way in which $(h_0 + 3x/2)^2(f_0 + x)$ varies differently with increase in x according as h_0 or f_0 is zero or both finite, and are due ultimately to the fact that the functions of hydrogen ions and ferrous ions in repressing the reaction are different.

There still remains the interesting fact that, even after corrections have been made for salt effect (p. 349), experiments in which ferrous iron is added initially seem to give slightly lower values for k_2 with increasing amounts of ferrous iron. No satisfactory explanation has been found for this behaviour. On the other hand, both k_1 and k_2 are far more satisfactory in experiments in which there is no initial ferrous iron (type II) than in those where there is no initial acid (type III), so that the equations used appear to be more satisfactory for relatively rapid increases of ferrous iron than of hydrogen ions.

With the object of gaining further insight into the mechanism and of obtaining an estimate of the extent to which hydrogen and ferrous ions are diminished owing to the existence of the complex,

six experiments were devised so as to correspond with the various conditions which might obtain in Expt. 2 after it had reached a certain stage. Initially it had $a = 0{\cdot}200$, $b/2 = 0{\cdot}100$, and the stage chosen was when 0·075 of the ferric iron had been reduced. At this stage, which was attained in 29·5 minutes, one would have $h = 0{\cdot}075 \times 3/2$ and $f = 0{\cdot}075$ if 3 and 2 atoms of hydrogen and iron respectively remained free in solution according to the stoicheiometric equation. The six experiments were chosen with the above values of a and b and with concentrations of h and f as shown :

Expt.	h.	f.							
20	0·1125	0·0750	corresponding	to	$3H^{\cdot}$	and	$2Fe^{\cdot\cdot}$	remaining	free.
24	0·0750	0·0750	,,	,,	$2H^{\cdot}$	,,	$2Fe^{\cdot\cdot}$	,,	,,
25	0·0750	0·0375	,,	,,	$2H^{\cdot}$	,,	$Fe^{\cdot\cdot}$	,,	,,
26	0·0375	0·0375	,,	,,	$H^{\cdot}$	,,	$Fe^{\cdot\cdot}$	,,	,,
31	0·1125	0·0375	,,	,,	$3H^{\cdot}$	,,	$Fe^{\cdot\cdot}$	,,	,,
32	0·0375	0·0750	,,	,,	$H^{\cdot}$	,,	$2Fe^{\cdot\cdot}$	,,	,,

As can be seen from the curves * (Fig. 1), the initial velocities are slower in the case of Expt. 20, and faster in all the others, than the reaction from the corresponding point in Expt. 2, the curve in the case of this experiment being plotted with the origin corresponding to the stage concerned. This would indicate that in Expt. 2 there are fewer hydrogen and ferrous ions opposing reaction than in Expt. 20, some being locked up in the complex. On the other hand, in Expt. 2 the complex is already at the concentration imposed by the stabilising effect of the reactions affecting it, whereas, in the earliest stages of the other reactions, it has probably not attained such a condition, so that comparisons are not rigid. Passing to the general course of the curves, it would appear that the conditions in Expt. 2 are such as would be expected from the repressing effect of approximately 2·7 moles of hydrogen ion and 1·7 moles of ferrous ion, for, considering the various values of t for constant values of x (which is the correct criterion), its curve is slightly farther from that of Expt. 20 than from a compromise between those of Expts. 24 and 31 which would approximately represent 2·5 and 1·5 moles respectively; as it is also about one-third of the way between those of Expts. 20 and 25, it would appear to correspond to 2·67 and 1·67 moles of hydrogen and ferrous ions respectively; both situations suggest that only about one-third of the hydrogen and ferrous ions which might possibly be locked up in the complex are actually so, or that two-thirds of the total complex formed have already broken down to final products.

Although the results in the foregoing discussion leave many details

* In these curves the extent of reduction (x) is plotted against time (t) which has been reduced in accordance with the correction for salt effect (p. 349).

in an unsatisfactory state, there is little doubt that the general conclusions are not far from the truth, and it is therefore of interest to compare them with certain other workers' views.

Raschig's ideas on the general course of the oxidation of hydroxylamine are put forward in detail in his "Stickstoff- und Schwefel-Studien," 1924. They are, briefly, that the first stage consists in the slow formation of the radical NH·OH, which unites with a similar radical to give $\begin{matrix}\mathrm{H{\cdot}N{\cdot}OH}\\ |\\ \mathrm{H{\cdot}N{\cdot}OH}\end{matrix}$. After this point a variety of possibilities is supposed to arise and the persistence of any one type of molecule will depend not only on its inherent stability but also on the rapidity with which it may be further oxidised. Thus, in the next phase one might have $\begin{matrix}\mathrm{N{\cdot}OH}\\ \|\\ \mathrm{N{\cdot}OH}\end{matrix}$ or $\begin{matrix}\mathrm{H{\cdot}N}\\ |\\ \mathrm{H{\cdot}N}\end{matrix}\!\!>\!\mathrm{O}$ according as the dihydroxyhydrazine could be further oxidised before it dehydrated or not, and in the latter case further oxidation would give hyponitrous acid, $\begin{matrix}\mathrm{H{\cdot}N}\\ |\\ \mathrm{HO{\cdot}N}\end{matrix}\!\!>\!\mathrm{O}$, which would decompose to nitrous oxide if nothing were present to oxidise it more rapidly than it could decompose. These views appear to the author to have the great advantage that they explain the variety and varying proportions of the end-products.

The results described herein, however, indicate that the first *measurable* stage involves, in effect, the removal of two hydrogen atoms from each molecule of hydroxylamine, because undoubtedly two molecules of ferric salt are implicated, and it is difficult to see what (if any) preliminary rapid reaction, save the formation of a "critical complex," could lead to a subsequent measurable termolecular reaction. The molecule thus appears to be oxidised to the stage represented by the hypothetical nitroxyl or nitrous oxide, although the latter is only produced as the result of secondary changes. These views agree, to a certain extent, with the earlier opinion expressed by Raschig, when dealing with the estimation of hydroxylamine by ferric salts, that an intermediate compound (possibly nitroxyl) of moderate stability is produced, which delays the completion of the reaction for analytical purposes (*Z. angew. Chem.*, 1904, **17**, 1411).

As will be seen from the experimental portion of this paper, there is no foundation for Brönsted's statement, quoted on p. 337, that the reaction under discussion is not appreciably susceptible to salt effect, although the magnitude is not so great as he appeared to look for. Actually there is a definite negative salt effect, which would, according to Brönsted, indicate reaction between ions of opposite polarity; but it is doubtful whether his hypotheses, which

are based on comparatively simple cases, can be extended to such complicated reactions as the present.

The hydroxylamine was always employed as hydrochloride, which had been recrystallised and freed from excess acid; both this salt and the ferric chloride would give a trace of free hydrochloric acid by hydrolysis, so that, in experiments with no added acid, there would always be a trace of free acid initially, which would slightly affect the earliest velocity coefficients.

Experimental.

All the experiments were carried out at 25°, with the exception of those necessary to find the temperature coefficient. Time is expressed in minutes throughout. The details call for no special description except in regard to the analytical method. The course of the reaction was followed by the estimation of unchanged ferric iron. The process was based on two facts: (1) hydroxylamine has no effect on iodine during the short time necessary for titrations provided that considerable mineral acid is present—sulphuric acid sufficient to be in normal concentration throughout the titration was found to fulfil this condition; and (2) ferric iron can be estimated consistently and fairly accurately by titration of iodine liberated from potassium iodide, if a trace of cuprous iodide is present as recommended by Hahn and Windisch (*Ber.*, 1923, **56**, 598). The equilibrium which tends to be set up ($Fe^{\cdots} + I' \rightleftharpoons Fe^{\cdot\cdot} + I$) is displaced by titration of iodine as fast as it is formed, and the presence of the cuprous salt accelerates the reaction (presumably by more rapid reduction of ferric salt and continuous re-formation of cuprous salt) to such an extent that titrations can be completed in the ordinary time instead of lasting for several minutes, as in the absence of cuprous salt. Although the method has been criticised (Rupp, *Apothek. Z.*, 1924, **39**, 422), the author's experience is that it is useful and gives results about 1 part in 300 parts high (with titres of 40 c.c.), but this error might be reduced if precautions were taken against the aerial oxidation of the solution containing hydriodic acid and ferrous salts.

The starch–iodine coloration returns after a few minutes in the titrations made during actual runs, and rather less rapidly in controls with ferric salts in the absence of reaction products. The difference is attributed to the presence of traces of nitrous acid.

As the result of many duplicate runs, it may be stated that experiments are reproducible almost invariably within about 0·1 c.c. on titres of usually 30 or 40 c.c.

The behaviour of a complex of the type suggested on p. 342 in such titrations is, of course, uncertain; it might react either as

ferrous or as ferric iron. The latter possibility is improbable, for the apparent rate of initial change would then be far less than the actual, and would subsequently tend to increase temporarily as the complex broke down; the apparent course of the reaction shows such enormous diminution in velocity that it is more likely that the complex reacts as a ferrous compound.

A control was made to ascertain whether hydroxylamine in nearly neutral solution exercised any oxidising effect on ferrous iron, such as it exerts in alkaline solution. The result was definitely negative.

The curves obtained by plotting experimental differential velocities against x change so rapidly that they are not capable of "smoothing." The velocities shown in the tables were therefore obtained by plotting x against the square-root or fourth-root of time, according to circumstances. The fairly flat curve thus obtained was smoothed and the values of $\sqrt{t}$ or $\sqrt[4]{t}$ corresponding to a series of values of x were read off, and, from the values thus obtained, a further curve was constructed, on the basis of $v = \delta x/\delta t$, showing the relation between x or $(a - x)$ and v. Even this method leaves considerable uncertainty in the early stages of experiments of type I. The integrated velocity coefficients are based on unsmoothed values.

Salt Effect.—Experiments similar to No. 4 were made with the addition of $M/10$- and $M/5$-ammonium sulphate; they gave results uniformly slower in the proportion 1·14 and 1·30, respectively. A similar experiment comparable with No. 2 gave a slightly greater depression. The primary object of this type of experiment was to find what correction, if any, should be applied to experiments of types III and IV (in which the ferrous salt had been added, for convenience, as ferrous ammonium sulphate), in order that they should be comparable with one another and with those of other types. When a definite effect was found, it was essential to make a few other determinations in order to obtain an estimate of that due to ferrous sulphate. An experiment parallel with No. 12, but having $M/10$-ammonium sulphate present, in addition to the $M/10$ already added as the double salt, showed a reduction of velocity in the ratio 1·17 to 1, whereas from the foregoing one would have expected a ratio of 1·30 to 1·14, *i.e.*, 1·14 to 1—a result which is as near as can be expected from the graphical methods which have to be used in the absence of really satisfactory velocity coefficients, and which shows that the salt effect is fairly consistent.

$M/15$-Aluminium sulphate gave a depression identical with that of $M/5$-ammonium sulphate and, therefore, twice as great as the $M/10$-ammonium sulphate to which it is equivalent; this result is characteristic of the ion of higher valency.

TABLE I.

< = values rising during expt. > = values falling during expt. (c) = approx. constant at value annotated.

Expt.		a.	$\frac{1}{2}b$.	h.	f.	$k_1 \times 10^5$. Integrated.	$k_1 \times 10^5$. Differential.	$k_2 \times 10^6$. Integrated.	$k_2 \times 10^6$. Differential.	% completed.
Type I.	1	0·200	0·0500	—	—	500>250	470>220	150<245	190<260	80
	2	,,	0·1000	—	—	500>200	350>200 (c)	160<240	230 (c)	50
	3	0·100	0·0500	—	—	800>360	500>370 (c)	140<265	210<260	60
Type II.	4	0·200	0·0500	0·1000	—	164>120	140 (c)	180<220	190<250	70
	5	,,	,,	0·2000	—	89 (c)	88 (c)	180<225	185<220	60
	6	0·100	,,	0·2000	—	89 (c)	89 (c)	180 (c)	180<210	35
	7	0·200	,,	0·8000	—	24 (c)	—	192 (c)	—	25
	8	0·100	0·0250	0·2000	—	84 (c)	84 (c)	170 (c)	170<200	50
	9	,,	0·0500	0·8000	—	22 (c)	—	176 (c)	—	10
	10	0·200	0·1000	0·8000	—	24 (c)	—	192 (c)	—	15
	11	0·040	0·0100	0·8000	—	21 (c)	—	168 (c)	—	10
	22	0·200	0·0500	0·0500	—	210>170	190>155	160<240	180<240	75
Type III.	15	0·200	0·0500	—	0·1000	85<260 (c)	65<270>240	0(?)<200	0<250	70
	23	,,	,,	—	0·0500	220<290>250	320>215	0(?)<215	115<230 (c)	75
Type IV.	12	0·200	,,	0·1000	0·1000	169 (c)	169 (c)	200<230	200<255	20
	13	,,	,,	0·1000	0·2000	140 (c)	145 (c)	150<182	170<230	30
	14	,,	,,	0·2000	0·1000	97 (c)	97 (c)	195<220	210<250	30
	17	,,	,,	0·0500	0·1000	195>170	200>140	110<190	110<195	60
	18	,,	,,	0·1000	0·0500	148 (c)	150>130	171<215 (c)	165<240	55
	19	,,	,,	0·0500	0·0500	240>180	240>155	145<210	150<215 (c)	60
	20	0·125	0·0625	0·1125	0·0750	140 (c)	138 (c)	170<190	160<215	25
	24	,,	,,	0·0750	0·0750	205 (c)	220>185	170<220	195<260	35
	25	,,	,,	0·0750	0·0375	222>200	220>190	192<260	190<290	55
	26	,,		0·0375	0·0375	330>260	310>220	195<245	180<255	55
	31	,,	,,	0·1125	0·0375	155 (c)	155 (c)	200<250	200<265	35
	32	,,	,,	0·0375	0·0750	250 (c)	255>220	120<200	145<230	35

Zinc ammonium sulphate was chosen as being best suited for comparison with the ferrous ammonium sulphate. For $M/5$- and M/10-solutions it showed depressions in the proportions 1·54 and 1·31 respectively. As these are consistent with the foregoing results, the general trend was adopted as the basis for corrections of all experiments of types III and IV, and the factors by which velocities are multiplied (or times divided) are :

for 0·2000	molar	ferrous	ammonium	sulphate	1·54
0·1000	,,	,,	,,	,,	1·30
0·0750	,,	,,	,,	,,	1·22
0·0500	,,	,,	,,	,,	1·14
0·0375	,,	,,	,,	,,	1·11

A comparison of, for example, Expts. 10 and 11 does not indicate the relatively large salt effect which might be expected from a five-fold change in the concentration of the tervalent ferric salt, and, for this reason, no attempt has been made to correct for such salt effect.

Experiment I. $a = 0{\cdot}2000$, $\frac{1}{2}b = 0{\cdot}0500$.

			Integrated.		Differential.	
t.	x.	$v \times 10^5$.	$k_1 \times 10^5$.	$k_2 \times 10^6$.	$k_1 \times 10^5$.	$k_2 \times 10^6$.
*0·33	0·0212	—	510	122	—	—
*0·83	0·0274	900	489	151	468	193
*1·50	0·0316	500	450	162	385	180
*2·17	0·0348	370	437	180	378	198
*3·67	0·0390	260	402	185	375	219
5	0·0432	190	—	—	382	247
*9·7	0·0480	125	346	198	360	259
12	0·0516	80	—	—	300	232
*20	0·0556	55	313	210	275	230
21	0·0570	50	—	—	277	237
30·5	0·0604	37	284	206	262	237
45	0·0650	25	289	230	250	240
70	0·0700	16	273	236	232	244
140	0·0780	8	252	247	223	260
160	0·0794	—	246	245	—	—
Experiment 5. $a = 0{\cdot}2000$, $\frac{1}{2}b = 0{\cdot}0500$, $h = 0{\cdot}2000$.						
*0·52	0·0042	—	91	182	—	—
*1·7	0·0074	193	92	191	88	186
*4·3	0·0114	107	94	198	84	182
6	0·0126	94	—	—	85	184
*8·6	0·0146	77·5	(82)	(176)	86	191
13	0·0178	60	—	—	88	202
*21	0·0220	42·5	88	197	87	203
23	0·0228	40	—	—	88	205
*38	0·0280	27	90	206	86	210
54	0·0316	22	—	—	89	220
*59	0·0326	20·5	87	204	88	220
91	0·0380	14·5	—	208	87	225
170	0·0470	8	89	224	82	220
284	0·0544	—	85	234	—	—
410	0·0596	—	84	224	—	—

* Indicates that these values are taken from an experiment at 15·5° and the time is corrected for the temperature coefficient.

Experiment 18. $a = 0{\cdot}2000$, $\frac{1}{2}b = 0{\cdot}0500$, $h = 0{\cdot}1000$, $f = 0{\cdot}0500$.

(All values of v, k_1, and k_2 should be multiplied by 1·14, the salt effect factor.)

5	0·0048	82·5	142	162	134	143
12	0·0098	63·0	134	145	133	152
23	0·0158	47·0	134	152	134	165
39	0·0222	32·8	134	161	128	171
76	0·0316	20·3	129	163	126	185
110	0·0374	14·7	128	174	122	190
171	0·0448	10·0	125	182	119	199
255	0·0518	6·8	123	189	116	207
320	0·0557	5·4	122	190	114	209

(The product hf increases four-fold, and h^2f seven-fold during the run.)

Summary.

1. The rate of reaction *after the early stages* is directly proportional to the concentration of hydroxylamine and to the square of that of ferric chloride, and inversely proportional to the concentration of ferrous salt and to the square of the hydrogen-ion concentration.

2. The most probable interpretation is that reaction proceeds by way of an intermediate equilibrium involving a complex of the type shown: $2Fe''' + NH_3OH^{\cdot} \rightleftharpoons Fe'' + 2H^{\cdot} + (NOH,Fe,H)''' \rightarrow N_2O$, etc.

3. The abnormal temperature coefficient of 6·5 for a 10° rise would thus be partly due to a more favourable displacement of the equilibrium.

4. "Salt effect" is negative—reaction velocity is depressed by the addition of indifferent salts.

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XLV.—*The Structure of the Normal Monosaccharides. Part IV. Glucose.*

By EDMUND LANGLEY HIRST.

IN Part I (Hirst and Purves, J., 1923, **123**, 1352) the reasons which had led to the general adoption of a butylene oxide formula for normal aldose derivatives were reviewed, the need of more definite chemical evidence was pointed out, and a method for studying the problem was outlined which has since furnished strong evidence that normal derivatives of xylose (*loc. cit.*), arabinose (Hirst and Robertson, J., 1925, **127**, 358), and rhamnose (Hirst and Macbeth, this vol., p. 22) are, in fact, amylene-oxidic and not butylene-oxidic, as had hitherto been supposed. In the experiments now to be

described, the method has been extended to the hexose series. The oxidation of tetramethyl glucose, whose structural relationship to the normal methylglucosides and to glucose has been the subject of much investigation, has been studied and as a result it appears that the amylene oxide formula should be ascribed also to normal derivatives of glucose. This is in exact agreement with evidence as to the structure of glucose recently obtained by Charlton, Haworth, and Peat (this vol., p. 89), whose experiments were based on considerations of an entirely different nature. If this structure for glucose be accepted, changes in the nomenclature of certain derivatives will obviously be necessary analogous to the renaming of normal tetramethyl glucose as the 2 : 3 : 4 : 6- instead of the 2 : 3 : 5 : 6-derivative of glucose.

The principal method adopted in the present investigation was to oxidise tetramethyl glucose with nitric acid. The reaction between a normal trimethyl pentose (I) and nitric acid is simple in nature, involving only the oxidation to carboxyl of the reducing and the potential primary alcoholic groups situated respectively at the two ends of the pentose carbon chain. Trimethyl rhamnose (II) also reacted simply, the terminal group ·CH(OH)·CH_3, produced by the action of the oxidising agent in forming trimethyl rhamnonic acid, giving quantitatively carboxyl and carbon dioxide. A methylated hexose, however, whether a 1 : 4- or a 1 : 5-oxide, presents a very different type of structure and it was to be expected that the course of oxidation would be more complicated. If the amylene-oxide structure of tetramethyl glucose (III) be assumed, the first stage in the reaction would be the production of tetramethyl gluconic acid (IV), and its subsequent course would be determined by the action of nitric acid on the group ·CH(OMe)·CH(OH)·CH_2·OMe, with the ketone ·CH(OMe)·CO·CH_2·OMe as a probable intermediate product. It is well known that ketones of the type R·CO·R′ may be oxidised in different ways according to the experimental conditions. The main product from 2 : 3 : 4 : 6-tetramethyl glucose might therefore be either *d*-dimethoxysuccinic acid (V) or inactive xylotrimethoxyglutaric acid (VI), according as the break occurred between the 4th and 5th or between the 5th and 6th carbon atoms. It is evident that by a similar series of steps, shown in the accompanying scheme, butylene-oxidic tetramethyl glucose (VII) might also give dimethoxysuccinic acid, and it follows that the isolation of this acid alone would not enable precise conclusions to be drawn concerning the structure of tetramethyl glucose. The detection of xylotrimethoxyglutaric acid, on the other hand, would definitely indicate the presence of an amylene-oxidic linking. It was therefore necessary to establish experimental conditions such that the nature of the

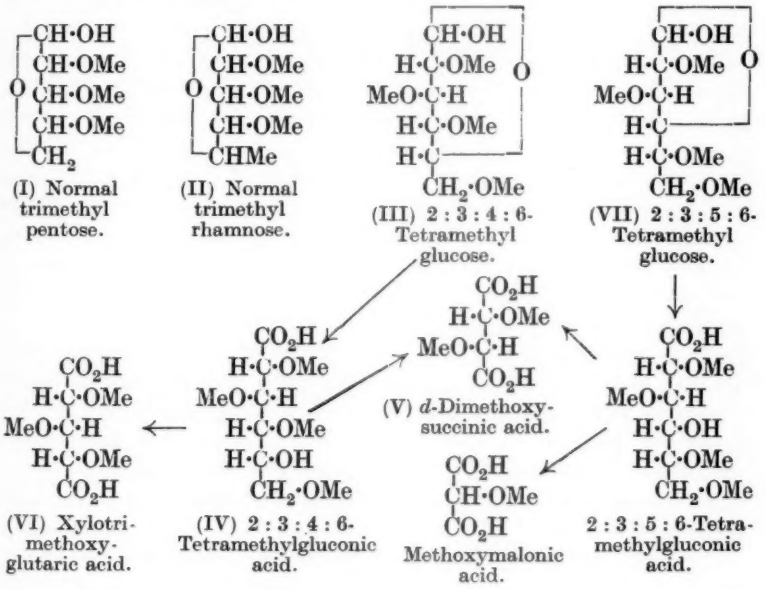
various oxidation products would lead definitely to the allocation of a structural formula.

This was ultimately accomplished by oxidising tetramethyl glucose for a short time with nitric acid of density 1·420. The reaction proceeded smoothly, was easy to control, and led to very little loss of material by side reactions. In this respect the reagent was much more satisfactory than the acid (*d* 1·2) which had previously been most frequently employed in the sugar group. With the latter, even at comparatively low temperatures, the more prolonged action necessary to effect the requisite oxidation invariably yielded considerable quantities of oxalic acid by a profound decomposition of the molecule. The product isolated in good yield was a mixture containing both *d*-dimethoxysuccinic acid and xylotrimethoxyglutaric acid, which were separated from each other by taking advantage of the different rates of formation of their very characteristic crystalline diamides. Dimethoxysuccinamide (Purdie and Irvine, J., 1901, **79**, 960) and xylotrimethoxyglutaramide (Hirst and Purves, *loc. cit.*) were thus obtained in a pure condition and their identity was placed beyond doubt by comparison with authentic specimens. It has already been indicated (Hirst and Macbeth, *loc. cit.*) that there appears to be no reason for suspecting any wandering of the methyl groups during oxidation, and it follows, therefore, from what has been said above, that normal tetramethyl glucose must be the 2 : 3 : 4 : 6-derivative possessing the amylene oxide formula (III), the possibility of a propylene or ethylene-oxide structure being entirely excluded by the nature of the products isolated.

The interest attached to this reaction and the desirability of accumulating as much evidence as possible concerning the oxidation of a fully methylated hexose led to a further study of the action of nitric acid and of alkaline potassium permanganate on tetramethyl glucose. The reaction appears to take an entirely different course from that of 2 : 3 : 6-trimethyl glucose when oxidised under precisely similar conditions (Irvine and Hirst, J., 1922, **121**, 1222). The latter gave with nitric acid (*d* 1·2) at 60° a dibasic acid (dimethylsaccharic acid), whereas tetramethyl glucose gives mainly tetramethylgluconic acid with a small quantity of dimethoxysuccinic acid, apparently without going through the intermediate stage of trimethylsaccharic acid. This difference is interesting, especially as butylene-oxidic trimethyl arabinose with a terminal group similar to that present in tetramethyl glucose can be oxidised to dimethoxyglutaric acid (Baker and Haworth, J., 1925, **127**, 365). A sufficient number of examples has not, however, been examined to justify any views as to whether this behaviour is the exception or the rule. Prolonged treatment of tetramethyl glucose with nitric acid (*d* 1·2)

at higher temperatures produces a complex mixture containing much oxalic acid and little or no trimethoxyglutaric acid, the chief constituent being dimethoxysuccinic acid. Oxidation with alkaline potassium permanganate gave oxalic acid and dimethoxysuccinic acid.

Summarising the evidence obtained from these experiments, it appears that the oxidation of amylene-oxidic tetramethyl glucose with nitric acid leads first to 2 : 3 : 4 : 6-tetramethylgluconic acid. Further oxidation splits the carbon chain either between the 4th and 5th or between the 5th and 6th carbon atoms to give dimethoxysuccinic acid or xylotrimethoxy-glutaric acid, and the relative proportions in which the two changes take place vary with the experimental conditions, the latter change being favoured by oxidation with stronger acid for a shorter time.


(I) Normal trimethyl pentose.
(II) Normal trimethyl rhamnose.
(III) 2 : 3 : 4 : 6-Tetramethyl glucose.
(VII) 2 : 3 : 5 : 6-Tetramethyl glucose.
(V) d-Dimethoxy-succinic acid.
(VI) Xylotri-methoxy-glutaric acid.
(IV) 2 : 3 : 4 : 6-Tetramethylgluconic acid.
Methoxymalonic acid.
2 : 3 : 5 : 6-Tetra-methylgluconic acid.

EXPERIMENTAL.

Stability of Dimethoxysuccinic Acid in Presence of Nitric Acid.—Dimethoxysuccinic acid was heated in nitric acid (*d* 1·42) for several hours at 100°. No oxidation and no change in the initial specific rotation, $[\alpha]_D$ + 69·5° ($c = 1·375$), were observed. Previous experiments have demonstrated the stability of trimethoxyglutaric acid.

Oxidation of Tetramethyl Glucose with Nitric Acid (d 1·42).—When a solution of tetramethyl glucose (5 g. of carefully recrystallised

material conforming to the accepted standards) in nitric acid (40 c.c.; *d* 1·42) was kept at room temperature, oxidation began after 5 minutes; thereafter the reaction was controlled by gradual heating in such a way that evolution of oxides of nitrogen never became rapid. After ½ hour, the temperature was raised to 90° and kept at this point for 2 hours; the evolution of gas had then almost ceased. Water (2 vols.) was added, and the excess of nitric acid removed by careful distillation at 40°/9 mm., with the addition of water in the usual manner. The dry oxidation product was a glass soluble with difficulty in methyl alcohol. It contained no oxalic acid. After esterification by boiling with methyl alcohol (50 c.c.) containing 4% of hydrogen chloride, the product was distilled under diminished pressure (for details of the method used, see previous papers). The main fraction (2·65 g.) was a colourless oil, b. p. 135—140°/10 mm. (bath at 150—155°), $n_D^{16°}$ 1·4375. The first and last fractions (0·4 and 0·8 g., respectively) showed $n_D^{20°}$ 1·4345 and 1·4416.

Examination of the Oxidation Product.—The main fraction was soluble in water and all the usual organic solvents. $[\alpha]_D = +31·5°$ in methyl alcohol ($c = 2·085$) and + 33° in aqueous ethyl alcohol ($c = 0·8$), and the characteristic change in rotation shown by lactones was not observed. The absence of lactonic substances was further shown by the compound titrating as an ester. The physical and chemical properties agreed most closely with those required for a mixture of 60% of methyl *d*-dimethoxysuccinate and 40% of methyl xylotrimethoxyglutarate (Found: C, 47·0; H, 7·05; OMe, 58·9; 0·106 g. required 9·0 c.c. of *N*/10-alkali for hydrolysis. Calc. for the above mixture: C, 47·2; H, 7·0; OMe, 60·9%; 9·5 c.c. The b. p., rotation, and refractive index are also in accord with this view. [Methyl *d*-dimethoxysuccinate has b. p. 135°/12 mm., $n_D^{20°}$ 1·4340, $[\alpha]_D + 81°$ in methyl alcohol ($c = 6·26$) (compare Purdie and Barbour, J., 1901, **79**, 971), and methyl xylotrimethoxyglutarate has b. p. 132°/12 mm., $n_D^{15°}$ 1·4402, and is optically inactive.]

Complete confirmation of these views was obtained by the formation in good yield of crystalline dimethoxysuccinamide and xylotrimethoxyglutaramide by the action of ammonia on the mixed esters. A solution of 1·0 g. in 8 c.c. of methyl alcohol saturated with dry ammonia began, after a few hours, to deposit crystals in characteristic, opaque, white tufts. These were collected at the end of 3 days, and after being washed with alcohol and ether and dried at 105° were found to be pure dimethoxysuccinamide (yield 0·36 g.). The substance was insoluble in cold organic solvents, but slightly soluble in water, in which the value $[\alpha]_D + 95°$ ($c = 0·80$) was observed. It sublimed in long needles on being heated in a vacuum

(compare Purdie and Irvine, *loc. cit.*), showed no definite m. p., but when heated fairly quickly showed the following sequence of changes: darkened at about 245°, melted partly with decomposition at 269°, and was completely decomposed at 276° (Found: OMe, 34·3. Calc., OMe, 35·2%). Its properties were in exact agreement with those of an authentic specimen of the amide prepared from methyl *d*-dimethoxysuccinate.

The mother-liquor of the dimethoxysuccinamide was kept for a further 4 days. Colour changes took place similar to those observed during the formation of xylotrimethoxyglutaramide (*loc. cit.*), and 7 days from the beginning of the experiment another crop of crystals began to be deposited as flat, transparent prisms, resembling xylotrimethoxyglutaramide in crystalline form. After 12 days, 0·25 g. was collected. This material showed a moderate solubility in water and could be recrystallised from an alcohol–ether mixture. It was optically inactive (tested in 2% solution in water). It melted in air to give a dark blue liquid, m. p. 194—195°, and at 194—195° when mixed with an authentic specimen of the glutaramide prepared from xylose (Found: C, 43·5; H, 7·4; OMe, 41·1. Calc.: C, 43·6; H, 7·3; OMe, 42·3%).

Further quantities of dimethoxysuccinamide were obtained by treating with ammonia in methyl alcohol the first and the last fraction. No oxamide could be detected.

Oxidation with Nitric Acid (d 1·2) *at* 75°.—A solution of 5·5 g. of tetramethyl glucose in 85 c.c. of nitric acid (*d* 1·2) was heated at 75° for 12 hours until the reaction appeared to be complete. The oxidation products (isolated as before after esterification) were (*a*) methyl oxalate (1 g.), (*b*) a clear yellow syrup (3·5 g.), b. p. 138—149°/9 mm. (bath at 150—156°), $n_D^{22°}$ 1·4415, $[\alpha]_D$ + 54° in alcohol (c = 1·348), $[\alpha]_D$ + 53° in aqueous alcohol (c = 0·50), decreasing to + 43°. This material on treatment with ammonia in methyl alcohol gave a small quantity of oxamide and much *d*-dimethoxysuccinamide. No xylotrimethoxyglutaric acid could be detected. The oxidation products under these conditions form a complex mixture, but consist principally of oxalic acid and dimethoxysuccinic acid. The high refractive index, the drop in rotation shown by the solution in aqueous alcohol, and the titration figures are in agreement with the view that some tetramethylgluconolactone was present in the main fraction (Found: C, 46·5; H, 6·6; OMe, 54·7%; 0·178 g. required 14·2 c.c. of *N*/10-alkali for hydrolysis, partly as lactone, partly as ester). The analysis of the corresponding lead salt is in accord with these views (Found: Pb, 50·0; OMe, 18·6%).

Oxidation with Nitric Acid (d 1·2) *at* 60°.—A solution of 7 g. of tetramethyl glucose in 50 c.c. of nitric acid (*d* 1·2) was heated at

85° until oxidation commenced, the temperature being then lowered to 60° and the reaction allowed to continue for 4½ hours. The product was treated in the way already described and was finally distilled. After a first fraction of 0·85 g., the greater part (4·0 g.) of the material was collected at 142—143°/9 mm. It could not be separated into its components by fractional distillation. The distillate was a neutral, clear syrup which developed acidity in contact with water; $n_D^{19°}$ 1·4526, $[\alpha]_D$ + 108° in benzene (c = 1·176). In water the initial value, $[\alpha]_D$ + 80° (c = 1·792), dropped rapidly to 64° after 28 minutes, 54·5° after 83 minutes, 45° after 158 minutes, and 39° after 280 minutes; the final value was 35°. This behaviour is characteristic of δ-lactones. Titration with alkali showed that the substance was partly lactonic and partly esteric in character. 0·1502 G. required (*a*) 5·0 c.c. of *N*/10-alkali as lactone, (*b*) 3·0 c.c. of *N*/10-alkali as ester (Found: C, 50·1; H, 7·5; OMe, 53·5%). 0·8 G. dissolved in 6 c.c. of methyl alcohol saturated with ammonia gave crystals of dimethoxysuccinamide (0·05 g.) in a few hours. These observations proved that the methyl ester of trimethoxysaccharolactone, if present at all, must have been there in very minute quantity, and the material under examination appeared to consist of 80% of tetramethylgluconolactone and 20% of methyl dimethoxysuccinate. This mixture requires C, 50·3; H, 7·5; OMe, 54·5% and 0·150 g. would require (*a*) 5·1 c.c. of *N*/10-alkali as lactone, (*b*) 2·9 c.c. of *N*/10-alkali as ester, whilst the b. p. and the initial and final values of $[\alpha]_D$ are in agreement with those expected.

(For the properties of dimethoxysuccinic acid derivatives, see Purdie and Irvine, *loc. cit.*; for those of tetramethylgluconolactone, see Pryde, J., 1924, **125**, 520; Charlton, Haworth, and Peat, *loc. cit.*)

Oxidation with Potassium Permanganate.—Tetramethyl glucose (5 g.) was dissolved in water (100 c.c.) rendered just alkaline with potassium hydroxide, and to the solution, heated at 75°, was added gradually potassium permanganate (25 g.) dissolved in hot water. The colour of the permanganate solution disappeared quickly at first, but very slowly towards the end. After filtering and passing carbon dioxide through the filtrate to remove free alkali, the solution was evaporated to small bulk at 50°/12 mm. The greater portion of the potassium was removed by means of perchloric acid and after elimination of the remaining water the product (partly free acid and partly potassium salt) was esterified with acid methyl alcohol. On isolating and distilling the ester, 0·6 g. was obtained as a first fraction. This was almost entirely methyl oxalate (the identity of which was confirmed by transforming it into oxamide). The main fraction

(2 g.) showed b. p. 130—135°/9 mm. (bath at 145°), $n_D^{20°}$ 1·4342, $[\alpha]_D$ + 43° (c = 1·68) in methyl alcohol [Found: OMe, 55·5; CO_2Me (by titration), 64%]. When it was treated with ammonia in methyl alcohol, oxamide was first formed followed by much dimethoxysuccinamide (50% by weight of the ester used; properties as above). It was evident, therefore, that the products were essentially oxalic acid and dimethoxysuccinic acid, the amount of trimethoxyglutaric acid being negligible.

The author wishes to record his thanks to Mr. J. M. Smith, M.Sc., of Armstrong College, for valuable assistance in preparing certain of the compounds required in this investigation.

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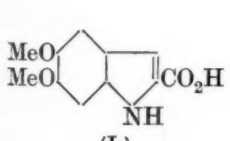
NEWCASTLE-UPON-TYNE. [*Received, December 12th*, 1925.]

XLVI.—3 : 4- *and* 2 : 5-*Dimethoxyphenylhydrazine.*

By WILLIAM HENRY PERKIN, jun., and LEON RUBENSTEIN.

IN a paper published a short time since (Blaikie and Perkin, J., 1924, **125**, 296; compare Kermack, Perkin, and Robinson, J., 1922, **121**, 1872), the synthesis was described of several derivatives of indole containing one methoxyl group in the benzene nucleus.

The present investigation was planned as a continuation of that research and it was hoped that it might be found possible to synthesise dimethoxy-derivatives of indole and to convert these into carbolines and indolediazines related to harmine and harmaline. We also desired to prepare and study more particularly such dimethoxy-derivatives of indole and tetrahydrocarbazole as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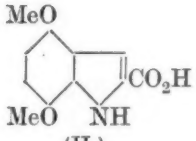
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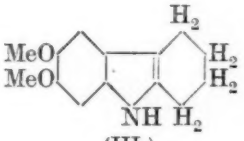

(III.)

and to compare their reactions with those of brucine with the object of obtaining further evidence bearing on the question of the positions of the methoxy-groups in that alkaloid (compare Lions, Perkin, and Robinson, J., 1925, **127**, 1159). Unfortunately, the preparation of phenylhydrazines of the type $(MeO)_2C_6H_3 \cdot NH \cdot NH_2$ required for these experiments, from the corresponding anilines, proved to be a matter of unusual difficulty, and it is probably for this reason, and

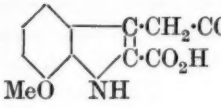
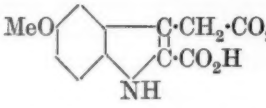
because they are so unstable when they have been obtained, that there is no mention of these important substances in the literature. These hydrazines, and especially the 2 : 5-dimethoxy-derivative, do not yield satisfactory condensation products with ketones such as *cyclo*hexanone or α-ketoglutaric acid and moreover the conversion of these hydrazones into the corresponding derivatives of indole or tetrahydrocarbazole by means of the usual acid reagents, alcoholic hydrochloric or sulphuric acid, glacial acetic acid, etc., is accompanied by the formation of so much tar that the preparation of these derivatives in any quantity was found to be impossible. Other methods must therefore be sought for the synthesis of these substances, and the present communication is confined to a brief description of the dimethoxyphenylhydrazines which have been prepared and of some indole and tetrahydrocarbazole derivatives which we have succeeded in obtaining in small quantities.

When 3 : 4-dimethoxyaniline hydrochloride (Fargher, J., 1920, **117**, 869) dissolved in acetic acid is treated with methyl nitrite, it yields brown needles of 3 : 4-*dimethoxybenzenediazonium chloride*, and this is converted by ammonium sulphite and ammonia into red crystals of *ammonium* 3 : 4-*dimethoxydiazobenzenesulphonate*. This salt is readily reduced by zinc dust to *ammonium* 3 : 4-*dimethoxyphenylhydrazinosulphonate*, the nearly colourless needles of which rapidly decompose on exposure and yield 3 : 4-*dimethoxyphenylhydrazine* (m. p. 81°) on treatment with sodium acetate. This very unstable substance combines with *cyclo*hexanone, and the syrupy hydrazone gives with alcoholic hydrochloric acid a small yield of 6 : 7-*dimethoxy*-1 : 2 : 3 : 4-*tetrahydrocarbazole* (III; m. p. 98°).

In a second series of experiments, 3 : 4-dimethoxyphenylhydrazine was condensed with ethyl pyruvate, and the syrupy hydrazone gave, with alcoholic hydrochloric acid, so small a yield of 5 : 6-*dimethoxyindole*-2-*carboxylic ester* (m. p. 172°; compare I) that the substance could not be further investigated. We next prepared 2 : 5-*dimethoxyphenylhydrazine hydrochloride* from 2 : 5-dimethoxyaniline hydrochloride (Mühlhausen, *Annalen*, 1881, **207**, 254) by a process similar to that just described in the case of the 3 : 4-derivative, and, on treatment with sodium acetate, this yielded 2 : 5-*dimethoxyphenylhydrazine* (m. p. 85°). Both the hydrochloride and the free base are, however, so unstable and condense with ketones with such difficulty that the investigation could not be continued.

Included in this communication is a brief account of 2-*carboxy*-7-*methoxyindole*-3-*acetic acid* (IV) and 2-*carboxy*-5-*methoxyindole*-3-*acetic acid* (V) obtained respectively by condensing *o*-methoxyphenylhydrazine and *p*-methoxyphenylhydrazine with α-ketoglutaric

acid and treating the products with alcoholic hydrochloric or sulphuric acid.

(IV.)   (V.)

On testing the various methoxy-derivatives described in this communication for the brucine reaction—the orange to red coloration produced on adding a drop of nitric acid to the solution of a trace of brucine in glacial acetic acid—it was found that the monomethoxyindole derivatives give only a yellow coloration. On the other hand, 6 : 7-dimethoxytetrahydrocarbazole (III) gives an immediate pink coloration which becomes deep red on warming and, in the case of 5 : 6-dimethoxyindole-2-carboxylic ester, the yellow colour produced at first becomes wine-red on warming. The behaviour of these substances seems to support the view of Lions, Perkin, and Robinson (*loc. cit.*, p. 1161) that brucine contains the two methoxyl groups in the *o*-position to each other.

EXPERIMENTAL.

3 : 4-*Dimethoxyphenylhydrazine*, $(MeO)_2C_6H_3{\cdot}NH{\cdot}NH_2$.—Finely powdered 3 : 4-dimethoxyaniline hydrochloride (20 g.; compare Fargher, *loc. cit.*) is added to glacial acetic acid (90 c.c.), and dried methyl nitrite passed into the well-stirred mixture, the temperature being maintained between 10° and 15°. The deep brown solution is poured into dry ether (500 c.c.), and the 3 : 4-dimethoxybenzenediazonium chloride thus precipitated in brown needles is immediately dissolved in ice-water and the solution added drop by drop and at 0° to a well-stirred, saturated ammonium sulphite solution (60 c.c.) containing ammonia (45 c.c.; *d* 0·880). The deep red product is kept for a few hours, and the red crystals (14 g.) of *ammonium* 3 : 4-*dimethoxydiazobenzenesulphonate* are collected (Found: N, 15·7; S, 12·0. $C_8H_{13}O_3N_3S$ requires N, 16·0; S, 12·1%). This substance is mixed with glacial acetic acid (10 c.c.), and zinc dust (3·7 g.) gradually added, the temperature being kept between 45° and 50°. The pale brown mixture is diluted with water, the zinc precipitated as sulphide and removed by filtration in an atmosphere of hydrogen sulphide to prevent oxidation. The yellow solution is concentrated by distillation under reduced pressure; *ammonium* 3 : 4-*dimethoxyphenylhydrazinosulphonate* (9·5 g.) then separates in greyish-white crystals with a metallic lustre (Found: N, 15·7; S, 12·0. $C_8H_{15}O_5N_3S$ requires N, 15·6; S, 12·1%).

This salt (12 g.) is boiled under reflux with alcoholic hydrochloric

acid (30 c.c. of 15%) for ½ hour. The mixture of 3 : 4-dimethoxyphenylhydrazine hydrochloride and ammonium chloride which separates from the deep red solution is collected, extracted with boiling alcohol, and filtered off; the filtrate deposits the hydrazine hydrochloride (4·5 g.) in grey prisms which, after recrystallisation from alcohol, melt at 162° (decomp.) (Found: N, 13·7. $C_8H_{13}O_2N_2Cl$ requires N, 13·7%). 3 : 4-*Dimethoxyphenylhydrazine hydrochloride* has a strong odour of the phenylhydrazine and must be rapidly dried on porous porcelain over sulphuric acid, since it readily decomposes in contact with air, becoming a dark mass. It gradually loses hydrogen chloride under reduced pressure and the crystals dissolve in water or alcohol to solutions which rapidly become red.

3 : 4-*Dimethoxyphenylhydrazine* separates, on the addition of sodium acetate to the aqueous solution of the hydrochloride, in colourless needles, m. p. 81°, which rapidly decompose in contact with air.

6 : 7-*Dimethoxytetrahydrocarbazole* (III).—3 : 4-Dimethoxyphenylhydrazine hydrochloride (2·5 g.) is added to alcohol (15 c.c.) containing *cyclo*hexanone (1·2 g.) and sodium acetate (1·4 g.). The mixture is boiled under reflux during 2 hours and poured into water; the hydrazone then separates as a syrup which does not solidify on standing or cooling. This syrup is washed with water, boiled with alcoholic hydrochloric acid (12 c.c. of 20%) for a few minutes, and the dark solution poured into water; the 6 : 7-*dimethoxytetrahydrocarbazole* that separates crystallises from dilute alcohol in pale yellow prisms, m. p. 98° (Found: C, 72·5; H, 7·6; N, 6·3. $C_{14}H_{17}O_2N$ requires C, 72·7; H, 7·4; N, 6·1%).

Ethyl 5 : 6-*Dimethoxyindole*-2-*carboxylate* (compare I).—3 : 4-Dimethoxyphenylhydrazine hydrochloride (2·5 g.) was added to a solution of ethyl pyruvate (1·2 g.) and finely powdered sodium acetate (1·3 g.) in alcohol (25 c.c.). After boiling for 2 hours, the red solution was diluted with water; the oily hydrazone that separated did not solidify on cooling. It was washed with water and boiled for a few minutes with alcoholic hydrochloric acid (10 c.c. of 20%); on adding water, *ethyl* 5 : 6-*dimethoxyindole*-2-*carboxylate* separated in a very crude condition. This was ultimately obtained pure, crystallising from alcohol in yellow prisms, m. p. 172° (Found: C, 62·5; H, 6·0; N, 5·7. $C_{13}H_{15}O_4N$ requires C, 62·7; H, 6·0; N, 5·7%), but the amount available did not allow of the preparation of the acid in a pure state.

2 : 5-*Dimethoxyphenylhydrazine*.—The diazotisation of 2 : 5-dimethoxyaniline in dilute aqueous hydrochloric acid was not feasible owing to the effervescence which accompanies the reaction even at low temperatures. Finely divided 2 : 5-dimethoxyaniline hydro-

chloride (20 g.; compare Mülhausen, *loc. cit.*) is added to glacial acetic acid, and dry methyl nitrite passed into the well-stirred mixture at 10°. The deep brown solution is gradually poured into dry alcohol-free ether with stirring; 2 : 5-dimethoxybenzenediazonium chloride is then precipitated in small, yellow needles and is very unstable. The ether is decanted, the crystals are rapidly washed with ether and dissolved in ice-cold water (60 c.c.), and the solution is added drop by drop to a well-cooled saturated solution of ammonium sulphite (60 c.c.) containing ammonia (40 c.c.; *d* 0·880). After remaining for a few hours, the deep red mixture is filtered, when *ammonium 2 : 5-dimethoxydiazobenzenesulphonate* remains as brick-red crystals. This substance may be crystallised from a little water, in which it is rather readily soluble (Found : N, 15·7; S, 12·1. $C_8H_{13}O_5N_3S$ requires N, 16·0; S, 12·1%). This sulphonate (26 g.) was mixed with glacial acetic acid (23 c.c.) and water (7 c.c.), and zinc dust (7·5 g.) added at 40—50°, a little at a time. The solution, which gradually became lighter in colour, was kept at 50° for an hour, diluted with water, the zinc removed as sulphide in an atmosphere of hydrogen sulphide, and the filtrate concentrated under reduced pressure; the *ammonium 2 : 5-dimethoxyphenylhydrazinosulphonate* (19 g.) that separated as a grey, crystalline solid was recrystallised from hot alcohol (Found : N, 15·6; S, 12·1. $C_8H_{15}O_5N_3S$ requires N, 15·6; S, 12·1%).

When this sulphonate (25 g.) was boiled under reflux with alcoholic hydrochloric acid (60 c.c. of 15%), a precipitate consisting of 2 : 5-*dimethoxyphenylhydrazine hydrochloride* and ammonium chloride separated from the deep purple solution. After a few minutes, the hydrolysis was complete, more alcohol was then added and some animal charcoal, the boiling liquid filtered and concentrated; the hydrazine hydrochloride was then obtained in colourless crystals (9·5 g.) which darken above 250° (Found : C, 48·2; H, 6·0; N, 13·8. $C_8H_{13}O_2N_2Cl$ requires C, 48·0; H, 5·9; N, 13·7%). This hydrochloride is very soluble in water and moderately soluble in alcohol and rapidly decomposes on exposure to air. 2 : 5-*Dimethoxyphenylhydrazine* separated in needles on the addition of sodium acetate to the aqueous solution of the hydrochloride; after drying on porous porcelain over sulphuric acid, it melted at 84°.

2-*Carboxy*-7-*methoxyindole*-3-*acetic Acid* (IV).—α-Ketoglutaric acid (25 g.; compare Blaise and Gault, *Compt. rend.*, 1908, **147**, 199) was dissolved in water (200 c.c.) containing sodium acetate (12 g.) and glacial acetic acid (10 c.c.), and *o*-methoxyphenylhydrazine hydrochloride (25 g.; Blaikie and Perkin, J., 1924, **125**, 315) in water (100 c.c.) then added. After the turbid solution had been

kept for a few hours, the yellow methoxyphenylhydrazone of α-ketoglutaric acid (35 g.) was collected. It separated from benzene in yellow prisms, m. p. 168° (decomp.).

This hydrazone (15 g.) was boiled under reflux with alcoholic hydrochloric acid (25 c.c. of 15%) for ½ hour. The hot, very dark coloured solution was filtered from the ammonium chloride, and the filtrate kept for several hours, crystallisation being assisted by occasional scratching. The crystals were collected, washed with small quantities of alcohol, and recrystallised three times from alcohol, from which *ethyl 2-carbethoxy-7-methoxyindole-3-acetate* separated in grey needles, m. p. 106°, b. p. 245—255°/11 mm. with slight decomposition (Found: C, 63·1; H, 6·0; N, 4·8. $C_{16}H_{19}O_5N$ requires C, 62·9; H, 6·2; N, 4·6%). This ester was boiled with 10% aqueous sodium hydroxide for 2 hours and the filtered solution acidified; the *2-carboxy-7-methoxyindole-3-acetic acid* that separated crystallised from alcohol in brown needles, m. p. 253° (decomp.) (Found by titration: equiv., 251. Calc. for a dibasic acid $C_{12}H_{11}O_5N$: equiv., 249).

2-Carboxy-5-methoxyindole-3-acetic Acid (V).—*p*-Methoxyphenylhydrazine (Blaikie and Perkin, *loc. cit.*; 9·6 g.), dissolved in water (20 c.c.) containing potassium acetate (6 g.), was boiled under reflux for 2 hours with a solution of α-ketoglutaric acid (8 g.) in a mixture of alcohol (30 c.c.) and water (5 c.c.). The product was filtered off and the alcohol evaporated; the *p-methoxyphenylhydrazone of α-ketoglutaric acid* then remained as an oil which did not solidify on cooling and rubbing. The oil was boiled under reflux with alcoholic sulphuric acid (25 c.c. of 20%), mixed with water and ether, the tar which had separated removed by filtration, and the ethereal solution washed with water, dried, and evaporated. Since the syrupy ester did not crystallise, it was boiled under reflux with sodium hydroxide (10%) for an hour, cooled, and acidified; a gum then separated which gradually hardened and after repeated recrystallisation from alcohol, *2-carboxy-5-methoxyindole-3-acetic acid* was obtained in pale yellow needles, m. p. 265° (Found: N, 5·9; equiv. by titration, 250. $C_{12}H_{11}O_5N$ requires N, 5·7%; equiv., 249).

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XLVII.—*The System Ferrous Oxide–Phosphoric Acid–Water and Some of its Oxidation Products.*

By Sydney Raymond Carter and Norman Holt Hartshorne.

In addition to the promised work (J., 1923, **123**, 2223) on the ferrous phosphates, this paper describes a study of the oxidation of some of the ferrous-phase complexes, which has thrown fresh light on the composition of the neutral ferric phosphates.

The following ferrous phosphates are described in the literature: $Fe_3(PO_4)_2,8H_2O$, or $3FeO,P_2O_5,8H_2O$, occurs in nature as *vivianite* and has been prepared by Becquerel (*Ann. Chim. Phys.*, 1833, **54**, 149), Debray (*ibid.*, 1861, **61**, 437), Horsford (*Sitzungsber. Akad. Wiss. Wien*, 1873, **67**, 466), and Evans (*Pharm. J.*, 1897, **4**, 141). $Fe_3(PO_4)_2,6H_2O$, or $3FeO,P_2O_5,6H_2O$, has been obtained by Gautier (*Compt. rend.*, 1893, **116**, 1491). Two acid phosphates are described, *viz.*, $FeHPO_4,H_2O$, or $2FeO,P_2O_5,3H_2O$, by Debray (*loc. cit.*), and $Fe(H_2PO_4)_2,2H_2O$, or $FeO,P_2O_5,4H_2O$, by Erlenmeyer (*Annalen*, 1878, **194**, 176). Kunz-Krause (*Ber. Deut. pharm. Ges.*, 1923, **33**, 20) describes a substance, containing ferrous and ferric iron and phosphoric acid, which is found in certain arable soils. This he assumes to be a basic ferrous ferric phosphate.

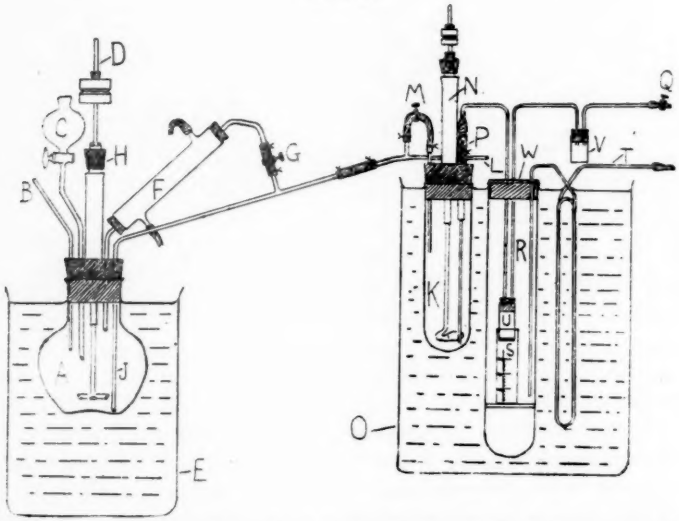
Experimental.

As in the case of the ferric phosphates (*loc. cit.*), the system was studied at 70°. The equilibrium mixtures were prepared by dissolving excess of Swedish iron wire (99·75% Fe) in solutions of phosphoric acid, obtained from the same source as that used in the ferric phosphate investigation. This operation, the subsequent stirring to attain equilibrium, and the collection of the liquid and solid phases were performed in an atmosphere of carbon dioxide in an apparatus (Fig. 1) in which the rubber stoppers were coated with paraffin wax or collodion and the connexions were made with thick-walled pressure tubing carefully wired on. The iron wire, in lengths of about ½ inch, was placed in the flask A, and the air in the apparatus was then displaced by passing carbon dioxide, admitted through the tube B, for about 2 hours, care being taken to clear all "pockets" such as stirrer bearings. The carbon dioxide was obtained from ordinary commercial cylinders and in some cases was sufficiently pure to be used directly, but in others the gas was passed through chromous chloride solution to remove the small quantity of oxygen present, then through sodium bicarbonate solution to remove hydrochloric acid, and finally

through strong sulphuric acid. (One sample of chromous chloride solution of about 250—300 c.c. was required for a series of experiments lasting several months and during this time no alteration in the characteristic blue colour of the solution was observed. We attribute this to the fact that the solution was kept in contact with amalgamated zinc, which appears effectively to regenerate the chromous chloride after it has been oxidised, hydrochloric acid, presumably, being formed.)

Phosphoric acid solution of the required strength, freshly boiled and still hot, was run into the flask through the tap-funnel C. The mixture was then stirred with the mercury-sealed stirrer, D,

FIG. 1.



until sufficient solid phase had formed, the flask being meanwhile maintained at approximately 70° by means of the water-bath, E, and undue evaporation of water prevented by the condenser, F. The stirrer was then stopped and its bearing sealed by the rubber stopper, H, to withstand pressure. By closing the clip, G, and admitting more carbon dioxide to the flask, a portion of the mixture was forced up the tube J and into the solubility tube, K, which was one of a series of four, the remainder (not shown) being connected, in a manner similar to K, to an extension of the tube L. By suitable adjustment of screw clips (*e.g.*, M) the mixture could be admitted to one or other of these solubility tubes, the displaced carbon dioxide escaping through the mercury seals, N, etc. The tubes were supported in the thermostat, O, fitted with a glass window and maintained at 70° $\pm$ 0·1° by an ordinary gas-regulator.

A suitable quantity of mixture having been transferred to K, the composition of the remainder in A was altered by the addition of a few c.c. of either water or syrupy acid and the next solubility tube was filled, and so on. Four mixtures of slightly different compositions were thus obtained from one sample of iron. The object in not dissolving the iron directly in the solubility tubes was to avoid the excessive frothing which occurred when this was attempted. The flask A was of such a shape and size that the froth could not rise : further the method ensured that the mixtures were free from undissolved iron which might have interfered with the collection of phase samples and would probably have rendered the attainment of equilibrium slow and uncertain.

The mixtures were stirred for at least a week, usually longer, and from the regularity of the results it is inferred that equilibrium had then been attained. In deciding the time allowed for stirring we had to be guided by our experience of the ferric system, since it would have been impracticable, on account of the risk of oxidation, to open the solubility tubes for the purpose of withdrawing samples for trial analyses. During the stirring the pressure of the carbon dioxide in the apparatus was maintained slightly above atmospheric in order to minimise the effect of leaks (great care, however, was taken to exclude these) and diffusion through the rubber connexions, and to counterbalance any reduction in pressure due to cooling caused by a fall in level of the thermostat water.

The apparatus for collecting the phase samples was essentially the same as that used in collecting the moist solid phase in the ferric system (*loc. cit.*), with the addition of arrangements for maintaining an atmosphere of carbon dioxide in and around the filter. The figure shows it connected to the solubility tube by means of the collecting tube P, which normally was closed with a piece of glass rod. Before this connexion was made, the collecting apparatus was cleared of air by a current of carbon dioxide admitted at Q, and the jacket, R, containing the weighing-bottle, S, was also cleared, by gas entering through the tube, T, the coiled portion of which, immersed in the thermostat, served to heat the gas and thus prevent cooling of the jacket. Connexion was then made as quickly as possible, the final arrangement being shown in the figure. By suitable adjustment of the gas pressure in different parts of the apparatus the mixture of liquid and solid phases was then blown over into the weighed filter, U (any overflow being caught in the trap, V), and was filtered. The liquid phase was caught in the weighing-bottle, S. During filtration an atmosphere of carbon dioxide was maintained in R by means of T, entry of air being minimised by the loose-fitting cork cover, W.

The liquid and moist solid phases were analysed by the methods used in the ferric system. In calculating the percentage of ferrous oxide, it was assumed that the whole of the iron was present in this state, although actually it was always found that the mixtures were oxidised to some extent, usually less than 1%. This point is discussed in the following section.

Analyses of the solid phases in the dry state were also made. The drying was accomplished in some cases by washing with dry ether alone, in an atmosphere of carbon dioxide. The apparatus used consisted of a filter flask in the neck of which a wide straight adapter and a tube for admitting carbon dioxide were supported by means of a rubber stopper. The side tube of the flask carried a mercury bubbler. A filter was made up in the adapter by means of two porcelain filter plates with a layer of asbestos between them, and the neck of the adapter was fitted with a rubber stopper carrying a tube for admitting carbon dioxide, a dropping-funnel, and a capillary tube which could be closed by a screw clip fitted to a rubber extension. The air was removed from the filter flask by means of carbon dioxide and with a steady stream of this passing through the filter, the moist solid was rapidly transferred to the adapter, the stopper carrying the dropping-funnel, etc., being removed as long as was necessary to accomplish this. The air was then quickly blown out of the adapter by carbon dioxide, the capillary tube serving as outlet. This was then closed and by increasing the pressure of the carbon dioxide as much liquid as possible was expressed from the moist solid. By alternately releasing and raising the pressure by operating the clip on the capillary tube, ether could be admitted from the dropping-funnel and forced through the solid.

In cases where ether could not readily be made to pass through the solid the following procedure was adopted. The solid was shaken for a few moments in a large weighing-bottle with water, containing two or three drops of concentrated hydrochloric acid (to remove any crust of ferric salt), which was then decanted and the process repeated with two or three washings of water, alcohol, and dry ether, respectively. The solid was finally dried in a stream of carbon dioxide.

Results.

The results are in Table I and are plotted by the triangular method in Fig. 2. Analyses of the dry solids are in Table II. In the second column of Table I figures are given for the percentage of iron present in the ferric state in some of the mixtures. This was determined by rapidly dissolving the contents of the overflow trap V (Fig. I) in water acidified with hydrochloric acid and

TABLE I.

Mixture.	% oxidation.	Liquid phase. $d_4^{15-20°}$.	Liquid phase. % FeO.	Liquid phase. % P_2O_5.	Moist solid phase. % FeO.	Moist solid phase. % P_2O_5.	Solid phase.
1	1·2	1·08	2·76	7·38	—	—	
2	—	1·16	4·38	12·06	34·9	35·51	
3	—	1·22	5·53	14·46	10·5	17·84	$2FeO,P_2O_5,5H_2O$.
4	1·6	1·20	5·48	14·96	35·9	36·0	
5	5·1	1·24	5·54	15·1	17·9	24·1	
6	—	1·31	7·71	21·6	—	—	
7	0·84	1·39	9·18	25·65	—	—	
8	—	1·43	9·88	28·25	—	—	$2FeO,P_2O_5,3H_2O$. Well-formed crystals, average length 0·1 mm.
9	—	1·53	10·99	32·78	—	—	
10	—	1·60	11·25	37·20	19·8	38·07	
11	—	1·60	11·29	37·21	21·3	39·13	
12	—	—	9·12	24·29	24·3	32·17	
13	—	1·42	10·1	27·20	21·9	32·47	
14	—	1·44	10·6	29·05	23·6	34·01	
15	0·87	1·45	10·6	29·46	23·2	33·39	$2FeO,P_2O_5,3H_2O$. Amorphous particles, average length 0·014 mm.
16	0·62	1·54	11·3	32·87	20·7	34·61	
17	0·92	1·55	11·5	33·99	26·3	37·81	
18	—	—	11·8	35·43	13·8	35·81	
19	2·75	1·60	11·9	36·99	—	—	
20	0·7	1·58	10·5	38·86	17·8	44·63	
21	—	1·60	8·77	41·52	18·8	46·84	
22	—	—	7·38	42·88	—	—	
23	—	1·61	6·29	46·61	16·2	48·10	$FeO,P_2O_5,4H_2O$.
24	—	1·63	4·87	50·49	12·7	50·38	
25	—	1·63	4·01	52·02	18·2	50·52	
26	4—6	1·71	3·15	57·51	15·2	53·12	

TABLE II.

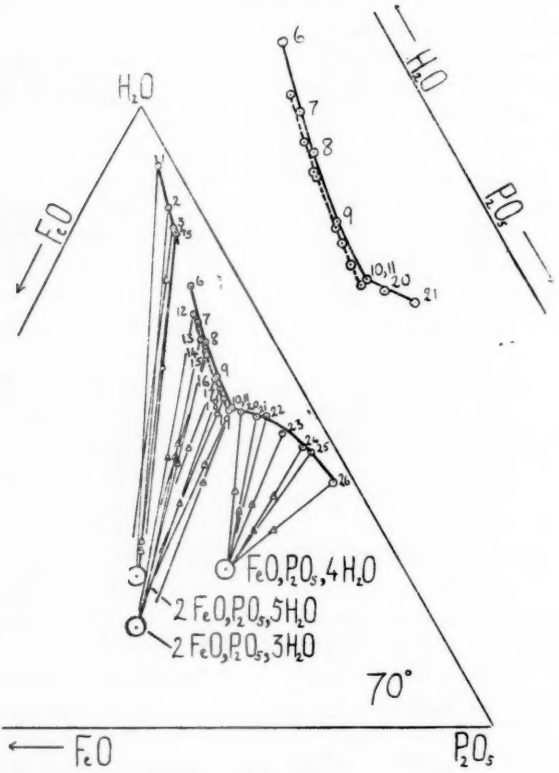
Analysis of Dry Solid Phases.

Mixture.	Found. % FeO.	Found. % P_2O_5.	Formula assigned.	Theoretical composition. % FeO.	Theoretical composition. % P_2O_5.
Specially prepared	38·0	37·8 38·0	$2FeO,P_2O_5,5H_2O$	38·3	37·8
9	41·6	41·7 40·7	$2FeO,P_2O_5,3H_2O$	42·4	41·8
22	24·8	49·5 49·7	$FeO,P_2O_5,4H_2O$	25·2	49·65

titrating a portion of the solution with potassium dichromate directly and then titrating another equal portion, after reduction by stannous chloride. The method gave only a very approximate value, since the first stages of oxidation are probably confined to the liquid phase (in the four-component system $FeO–Fe_2O_3–P_2O_5–H_2O$ the ferrous salts must have some region of existence as solid phases in the presence of ferric iron) and the samples taken consisted of both solid and liquid phases in varying relative amounts.

Moreover, an appreciable degree of oxidation probably occurred before the first titration could be completed. The figures were useful, however, as a rough test of the inertness of the atmosphere maintained over the mixtures during stirring. The high values given by mixtures 5 and 26 were due to the use of carbon dioxide which was subsequently found to contain 1% of oxygen. As already stated, the oxidation was neglected when the ferrous oxide

FIG. 2.



percentages were being calculated, since any attempt to determine the oxidation in liquid and moist solid phases separately, and make the necessary allowances, would have increased the already great difficulties in collecting the phase samples, besides being fraught with uncertainty as to whether the results would really represent the condition before the solubility tubes were opened. As justification for our procedure we may point to the regularity with which most of the solubility points lie on smooth curves and to the evidence afforded by the conjugation lines for the composition

of the solid phases, this evidence being confirmed by analysis of the dry solids.

The third column in Table I gives the densities of the liquid phases. The values were obtained by comparing the weights of the samples with their volumes at room temperature, estimated to 0·25 c.c. by the graduations on the side of the weighing-bottle S (Fig. 1). Since the average volume of a sample was near 20 c.c., the figures are accurate to about 1 part in 80.

With regard to the solid phases, within the range of acid concentrations studied, no neutral salt such as vivianite exists. It probably has a small range of existence in the region below the point corresponding to 7·38% P_2O_5 of mixture 1, but we have found it impossible to study this region on account of the increased susceptibility to oxidation which occurs as the acid concentration diminishes. Starting with the dilute-acid region, the first solid phase found, $2FeO,P_2O_5,5H_2O$, or $FeHPO_4,2H_2O$, has, as far as we are aware, not been described before. Its composition is confirmed by the analysis of the dry solid (Table II) and its crystalline form is shown in the photomicrograph reproduced in Fig. 3. We are indebted to Dr. Leonard Hawkes, Head of the Geology Department at Bedford College, for the following crytallographic analysis under the microscope. Biaxial; positive; axial angle $2V_\gamma =$ *ca.* 60—70°; dispersion of optical axis $\rho > \nu$ (?); optical axial plane parallel to the length axis of the prism. Examination was rendered difficult on account of the elongated habit and consequent tendency to settle on the slide in one position only.

The next solid phase, $2FeO,P_2O_5,3H_2O$ or $FeHPO_4,H_2O$, was described by Debray (*loc. cit.*), but doubt was subsequently cast on this author's work by Erlenmeyer (*loc. cit.*). We, however, have confirmed its existence both by the graphical method and by analysis of the dry solid (Table II). The figures are not so satisfactory as the analyses of the other dry solids owing to the very small amount of material available, but they are sufficiently conclusive. We have obtained it in two distinct forms which have slightly different solubility curves. This is shown clearly in Fig. 2, where this portion of the isotherm is drawn separately on an enlarged scale. The form showing the greater solubility is very finely divided and the particles are almost destitute of crystalline form while showing a characteristic elongated shape. A specimen of those in equilibrium with mixture 16 is shown in Fig. 4. The average length of the particles in this photomicrograph, which may be taken as representative of the whole series, is estimated to be 0·014 mm. Evidence for the composition of this solid is based solely on the conjugation lines, since all efforts to dry the

solid failed, no doubt on account of its extremely fine state of division.

The form showing the lower solubility is definitely crystalline. The type of the crystals in equilibrium with mixtures 9, 10, and 11 is shown in Fig. 5. The crystals are plates having, usually, six sides. The average diameter of those in the figure, measured in the direction of greatest length, is about 0·1 mm. Evidence for the composition of this form is based chiefly on the analysis of the dried solid in equilibrium with mixture 9 (Table II), the evidence of the conjugation lines from mixtures 10 and 11, which apparently lie at an invariant point, being inconclusive.

Mixtures 6, 7, and 8 gave a crystalline solid phase which was quite unlike any of the others in appearance. Unfortunately in no case was there sufficient material for analysis. The crystals are shown in Fig. 6. From the position of the liquid-phase points on the diagram (Fig. 2) we have concluded that it is another habit of the crystalline compound $2FeO,P_2O_5,3H_2O$ and accordingly have included the analytical figures in that section of Table I. The average length of the crystals (Fig. 6) was about 0·1 mm.

It appeared at first that the deposition of one form or the other was fortuitous. Subsequent perusal of the experimental notes showed, however, that in those cases where a suitable mixture (*i.e.*, one having convenient proportions of solid and liquid phases) was obtained at once in the reaction flask A (Fig. 1) and was transferred immediately to the solubility tubes, the more soluble form was obtained, whereas if further additions of iron or phosphoric acid solution were necessary, or if during the dissolution of the iron the temperature was raised or lowered (as was sometimes done to break up cakes of solid formed over-night in the reaction flask, or for other practical reasons), then the less soluble crystalline form resulted. Qualitative observations have shown that the salt has a very small temperature coefficient of solubility; moreover, its solubility is not greatly altered by varying the concentration of acid (see Fig. 2). If we assume that the molecules aggregate much more rapidly than they subsequently arrange themselves to form crystals, it is clear that the form first deposited will be an irregular aggregate, *i.e.*, an amorphous or quasi-amorphous solid. Moreover, since the solubility is scarcely affected by temperature and concentration, the aggregates may remain undisturbed for a long period unless these conditions are altered considerably. The aggregated form has more free energy than the crystalline variety and will be metastable and more soluble. The theory that the difference in solubility is connected in any way with the difference in particle size (given above) may be dismissed,

since the particles were probably too large for this factor to be operative (compare Hulett, *Z. physikal. Chem.*, 1901, **37**, 385, who found differences in the solubility of particles of diameter 0·002 mm. and less) and in any case the mixtures were stirred sufficiently long (8, 10, and 33 days) for the larger particles to grow at the expense of any small enough to give an abnormal solubility.

The solid phase in the mixtures richest in acid was the compound $FeO,P_2O_5,4H_2O$ or $Fe(H_2PO_4)_2,2H_2O$, described by Erlenmeyer (*loc. cit.*). Its composition is amply confirmed both by the conjugation lines (Fig. 2) and by analysis of the solid in equilibrium with mixture 22 (Table II). Typical crystals are shown in Figs. 7 and 8. It has a positive temperature coefficient and crystallises spontaneously within 24 hours from appropriate liquid phases which are allowed to cool to room temperature.

The colour of the liquid phases throughout the isotherm was the pale green characteristic of the ferrous ion. The solids were also pale green. The formation of complexes, which takes place in the ferric system, does not therefore appear to occur here.

Oxidation of the Mixtures.

It has already been stated that the mixtures poor in acid were particularly susceptible to oxidation. This showed itself in the formation of reddish-brown crystals which were deposited to a greater or less extent after the mixtures had been stirred for some days, and appeared to exist in stable contact with the ferrous phosphate already present. In mixture 1, the solid phase consisted almost entirely of these crystals and therefore it was obviously useless for the purpose of the ferrous isotherm to analyse the moist solid. It was, however, of interest to find out the composition of the crystals and it was fortunately found possible to separate them from admixed ferrous phosphate by the brief action of dilute hydrochloric acid. This was discovered by watching the behaviour of the mixture under the microscope, when, on adding a drop of hydrochloric acid, the ferrous phosphate dissolved almost immediately while the brown crystals appeared to be unaltered. The solid was therefore washed, by shaking with dilute hydrochloric acid for some minutes, transferred to a filter, and washed under pressure successively with a little more dilute acid, water, alcohol, and dry ether. A little of the solid, immediately dissolved in hydrochloric acid, gave only a very faint response to the test for ferrous iron. It was therefore not a ferroso-ferric phosphate. It gave a strong ferric reaction. Analysis of the remainder gave Fe_2O_3, 42·2; P_2O_5, 37·7. $Fe_2O_3,P_2O_5,4H_2O$ requires Fe_2O_3, 42·8; P_2O_5, 38·0%, and $Fe_2O_3,P_2O_5,4{\cdot}25H_2O$ requires Fe_2O_3, 42·3;

P_2O_5, 37·5%. The result thus agrees very closely with the latter formula, but we consider that, failing further evidence, it is better to regard it as incompletely dried $Fe_2O_3,P_2O_5,4H_2O$.

The naturally occurring strengite has this composition, and Erlenmeyer (*loc. cit.*) claims to have prepared a neutral phosphate of this composition; his analytical figures, however, are not very conclusive, as we pointed out in our earlier paper. Crystals of our compound are shown, as dark, rectangular prisms, side by side with ferrous phosphate in Figs. 3 and 6.

Since in the ferric system we had not observed a solid which resembled these brownish-red crystals in appearance, it seemed evident that they were only stable in the presence of ferrous iron and that if oxidation were completed, the solid would change. To test this point, a mixture was prepared in the region of existence of $2FeO,P_2O_5,5H_2O$ and was stirred at 70° in a solubility tube, the bearing of which was not sealed by mercury. From time to time the solid phase was examined microscopically, and the liquid tested for ferrous iron. Water was added as required to make up for loss due to evaporation through the stirrer bearing. The brown ferric salt was present from the first, and after 8 days constituted the whole of the solid phase, all the greenish-white, ferrous phosphate having disappeared. The liquid phase, however, still showed a strong ferrous reaction. After a further 8 or 9 days the brown colour of the solid had given place to a pale pink shade, resembling that of the ferric phosphates encountered in our previous work. Under the microscope, the solid was seen to be very much broken but definitely crystalline, many of the crystals having a characteristic kite-like shape. These are shown in Fig. 9, where a well-formed specimen will be seen in the middle of the picture. At this stage the liquid phase still showed a fairly strong ferrous reaction. Stirring was continued for another week without any change occurring in the appearance of the solid, but the liquid phase now gave a very weak ferrous reaction. The mixture was then left unstirred for another fortnight; it was then completely oxidised. It was stirred for a few hours to ensure equilibrium and the liquid and the solid (dry) were analysed. The liquid contained a trace of Fe_2O_3 and 7·09% of P_2O_5. The solubility curve of the ferric phosphates (*loc. cit.*, p. 2230) shows that the quantity of Fe_2O_3 corresponding to 7·09% P_2O_5 is measurable, being about 0·1%. This slight difference in solubility may, however, be attributed to the solid in that case having been amorphous, whereas here it was crystalline, and therefore we conclude that the same compound was concerned in both cases. The reason for obtaining the crystalline form by oxidation of a ferrous mixture

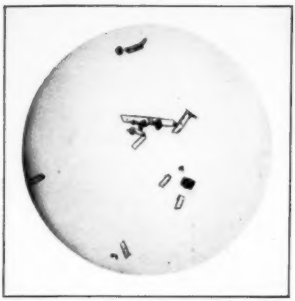


FIG. 3.—$2FeO,P_2O_5,5H_2O$ and β-$Fe_2O_3,P_2O_5,4H_2O$ (short dark prisms). ×10.

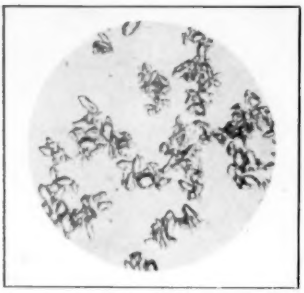


FIG. 4.—$2FeO,P_2O_5,3H_2O$ ("amorphous") × 160.

FIG. 5.—$2FeO,P_2O_5,3H_2O$ (crystalline). × 57.

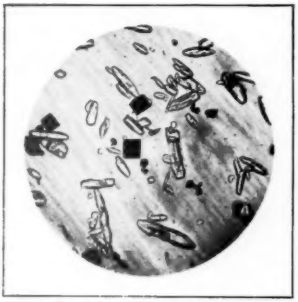


FIG. 6.—$2FeO,P_2O_5,3H_2O$ (crystalline) and β-$Fe_2O_3,P_2O_5,4H_2O$ (short dark prisms). × 50.

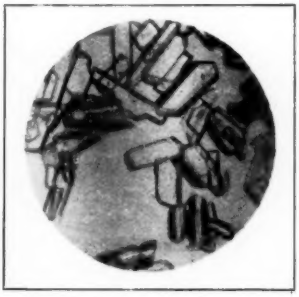


FIG. 7.—$FeO,P_2O_5,4H_2O$. × 25-50.

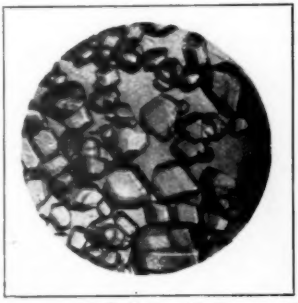


FIG. 8.—$FeO,P_2O_5,4H_2O$. × 43.

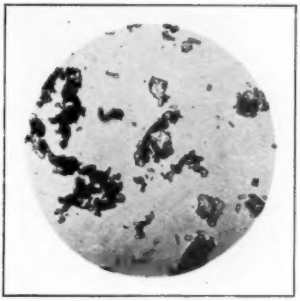


FIG. 9.—α-Fe_2O_3 $P_2O_5,4H_2O$. × 90

[*To face page* 372.]

probably lies in the gradual decrease in solubility which occurs during the process or in other factors inherent in it, which affect the velocity of crystallisation as opposed to aggregation and are evidently absent or suppressed when ferric oxide is treated with dilute phosphoric acid.

Analysis of the solid phase gave Fe_2O_3, 42·25; P_2O_5, 37·5, 37·6%, which, within the probable limits of experimental error, is the same as the composition found for the brown crystals. There are thus two neutral ferric phosphates having the composition $Fe_2O_3,P_2O_5,4H_2O$ in the four-component system Fe_2O_3–FeO–P_2O_5–H_2O at 70°. We will call the pink the α-form and the brown the β-form. Under the conditions studied, the α-form is stable in the absence, or in low concentrations, of ferrous iron, whilst the β-form exists in the presence of medium to quite high concentrations: indeed, judging from the readiness with which it crystallises from ferrous mixtures, in spite of all efforts to maintain an inert atmosphere, it may be inferred that in this region the range of existence of solutions in equilibrium with a ferrous salt only is very limited.

The difference between the α- and the β-salt may be explained in a similar way to that applied in the case of the neutral ferric phosphates at 25° (*loc. cit.*). As we mentioned there, the work of Weinland and Ensgraber showed that the pink ferric phosphates were probably complex ferri-phosphates. Thus we may suppose that the pink α-form has the constitution $[Fe(PO_4)_2]Fe,4H_2O$, while the brown β-salt is a true ferric phosphate, $FePO_4,2H_2O$. Support for the latter supposition is given by the colour changes which ferrous phosphate solutions undergo on oxidation: the original green colour changes to brown and finally to pink. The intermediate brown colour may well be due to the ferric ion, and it is the β-form which can exist at this stage.

It is now seen that we were in error in our earlier work in attributing five molecules of water to the solid phase in equilibrium with the weakly acid solution at 70°. That such a hydrate does exist appears to have been confirmed by Weinland and Ensgraber, and in our own work at 25° there seems to be little doubt that it was present. At 70°, however, the α-salt with four molecules of water is stable, at least in the region in which the above oxidation experiment terminated.

Summary.

1. The system FeO–P_2O_5–H_2O has been studied at 70°, between the concentrations 7·38 and 57·51% P_2O_5. Within this range the stable solid phases are the acid salts $2FeO,P_2O_5,5H_2O$, $2FeO,P_2O_5,3H_2O$, and $FeO,P_2O_5,4H_2O$, the first of which has, as far as is known, not been described before.

2. By the oxidation of phases poor in acid, two neutral ferric phosphates, both having the composition $Fe_2O_3,P_2O_5,4H_2O$, are deposited. The brown β-form exists in contact with liquid phases having high to medium concentrations of ferrous iron; at lower concentrations, the pink α-form becomes stable.

The authors wish to express their indebtedness to Dr. J. F. Spencer for much helpful advice and to Mr. A. Watson for carrying out many of the analyses.

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XLVIII.—*Condensations involving Reactive Methyl Groups in Heterocyclic Bases.*

By JAMES ERNEST HUMPHRIES.

THE reactions described below, *viz.*, the condensation of quinaldine, *p*-toluquinaldine, and α-picoline and of their quaternary salts with Michler's hydrol and a nitrosoamine, are further examples of the reactivity of methyl and methylene groups towards the groups :C:O and ·N:O. Fosse (*Ann. Chim. Phys.*, 1906, **8**, 18) found that, in presence of acetic acid as condensing agent, Michler's hydrol (4 : 4′-tetramethyldiaminobenzhydrol) reacted with the methylene group of such compounds as acetoacetic ester, acetylacetone, etc. Quinaldine and α-picoline condense readily with the hydrol under the same conditions, yielding the compounds

$C_9H_6N\cdot CH_2\cdot CH(C_6H_4\cdot NMe_2)_2$ and $C_5H_4N\cdot CH_2\cdot CH(C_6H_4\cdot NMe_2)_2$.

The condensations can also be effected by zinc chloride. The methiodides of the heterocyclic bases react more readily than the bases themselves and under conditions in which the latter are not affected, *viz.*, in alcoholic solution. The condensation products are similar to the *leuco*-compounds of the triphenylmethane dyes and are readily oxidised by lead peroxide and acetic acid to red dyes.

The quaternary salts do not react with benzenediazonium sulphate, but condense readily with *p*-nitrophenylnitrosoamine, in cold alcoholic solution. The resulting compounds were phenylhydrazones, *e.g.*, $C_9H_6N(MeI)\cdot CH:N\cdot NH\cdot C_6H_4\cdot NO_2$. This reaction differs from that of Adams (*Chem. Zentr.*, 1923, **94**, I, 1591), who added simultaneously solutions of potassium hydroxide and diazotised aniline to an aqueous solution of quinaldine methiodide and obtained the azo-compound, $C_9H_6N\cdot CH_2\cdot N:N\cdot C_6H_5$.

The bases themselves and their hydrochlorides do not react with

the nitrosoamine, so that in both reactions the reactivity of the α-methyl group is enhanced by converting the tertiary base into a quaternary compound.

EXPERIMENTAL.

Condensations with Michler's Hydrol.—(1) *Quinaldine.* A solution of equimolecular quantities of the hydrol and quinaldine in glacial acetic acid was warmed on a water-bath until the intense blue colour changed to deep red (1 hour). Ammonium hydroxide then precipitated a dark green oil which, isolated by means of ether, was obtained in pale-yellow needles, m. p. 131° (Found: N, 10·7. $C_{27}H_{29}N_3$ requires N, 10·6%).

The condensation product (1 mol.) was dissolved in hydrochloric acid (3 mols.) and enough water to make a 2% solution; acetic acid (2 mols.) was added and the whole cooled to 0°. Then, with rapid stirring, freshly prepared lead peroxide (1 mol.) was quickly added. The solution became intensely red. The lead was removed as sulphate, and the oxidation product obtained by addition of sodium hydroxide and extraction with chloroform. A red, amorphous powder was precipitated from the dried chloroform extract on adding ether. The *oxalate* was analysed (Found: N, 8·0. $C_{30}H_{32}O_6N_3$ requires N, 7·95%).

The oxidation product dyes silk violet. Its salts are red, but the pseudo-base, $C_9H_6N{\cdot}CH{:}C(C_6H_4{\cdot}NMe_2)_2$, is brown.

(2) p-*Toluquinaldine.* The condensation product (m. p. 152°) was similar to that formed from quinaldine (Found: N, 10·1. $C_{28}H_{31}N_3$ requires N, 10·3%).

(3) α-*Picoline.* The condensation was carried out as in (1) and pale yellow crystals, m. p. 187°, were obtained (Found: N, 12·1. $C_{23}H_{27}N_3$ requires N, 12·2%).

(4) p-*Toluquinaldine methiodide.* The condensation, which also proceeds in glacial acetic acid, was effected by boiling an alcoholic solution of the reactants for a few minutes. On concentrating the solution, copper-red needles, m. p. 160° (decomp.), were obtained (Found: I, 23·2; N, 7·6. $C_{29}H_{34}N_3I$ requires I, 23·05; N, 7·6%).

The corresponding methochloride, obtained by condensing *p*-toluquinaldine methochloride and the hydrol, was oxidised as in (1), but the deep-red, amorphous dye which was formed could not be obtained pure.

Condensations with p-*Nitrophenylnitrosoamine.*—When equal molecular quantities of benzenediazonium sulphate and *p*-toluquinaldine methiodide were mixed in alcoholic solution at the ordinary temperature, the solution turned red and golden-yellow plates, m. p. 133°, of the *periodide* of *p*-toluquinaldine methiodide

immediately began to separate (Found: N, 2·55; I, 69·1. $C_{12}H_{14}NI_3$ requires N, 2·5; I, 68·9%). This was readily reduced to the methiodide by sulphur dioxide or stannous chloride, and was also formed by warming the methiodide and iodine in glacial acetic acid.

No condensation took place when the methiodide was replaced by the methonitrate of *p*-toluquinaldine.

(1) p-*Toluquinaldine methiodide*. The nitrosoamine was prepared by Schraube and Schmidt's method (*Ber.*, 1894, **27**, 514). Equimolecular quantities of the nitrosoamine and the methiodide, each in alcoholic solution, were mixed at 0°. The crystalline precipitate was recrystallised from methyl alcohol, reddish-brown needles, m. p. 244°, being thus obtained (Found: N, 12·3; I, 28·6. $C_{18}H_{19}O_2N_4I$ requires N, 12·5; I, 28·35%).

That the new compound was the p-*nitrophenylhydrazone* of 2-formyl-6-methylquinoline was proved in the following way. *p*-Toluquinaldine methiodide was condensed with *p*-nitrosodimethylaniline (Kaufmann and Vallette, *Ber.*, 1912, **45**, 1738), yielding the Schiff's base, $C_{10}H_{10}N(MeI)\cdot CH{:}N\cdot C_6H_4\cdot NMe_2$, in green needles, m. p. 207 (decomp.). This was hydrolysed by boiling with dilute hydrochloric acid, and *p*-nitrophenylhydrazine added. The hydrazone so found was identical with the product of the nitrosoamine condensation.

(2) *Quinaldine methiodide*. The product formed red needles, m. p. 250° (Found: I, 29·4. $C_{17}H_{15}O_2N_4I$ requires I, 29·3%).

(3) *Quinaldine ethiodide* gave red needles, m. p. 262° (Found: I, 28·5. $C_{18}H_{17}O_2N_4I$ requires I, 28·3%).

(4) α-*Picoline methiodide* gave yellow needles, m. p. 260° (Found: I, 33·4. $C_{13}H_{13}O_2N_4I$ requires I, 33·1%).

In the last three cases the identity of the product was confirmed as in the case of (1).

The author wishes to thank Dr. W. H. Mills, F.R.S., for his valued advice.

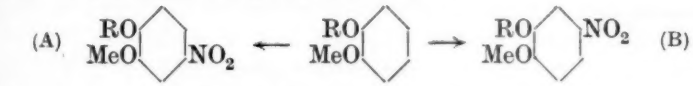
UNIVERSITY OF ABERDEEN. [*Received, December 15th*, 1925.]

XLIX.—*The Relative Directive Powers of Groups of the Forms* RO *and* RR'N *in Aromatic Substitution. Part I.*

By JAMES ALLAN and ROBERT ROBINSON.

THE nitration of veratrole in cold acetic acid solution proceeds extremely smoothly and 4-nitroveratrole is obtained in almost theoretical yield. Careful search reveals no trace of 3-nitro-

veratrole or of 4 : 5-dinitroveratrole in the product. An ether of guaiacol, other than veratrole, will naturally yield two nitro-derivatives in relative amounts which depend on the ratio of the directive powers of the groups RO and MeO.



Since the meta-directing influence of the alkyloxy-group is zero, we may assume that Directive Power of OR/Directive Power of OMe = % of (A) formed in the reaction/% of (B) formed in the reaction. In order to obtain numbers which can be compared, the directive power of MeO is taken to be 100. In every case nitration was carried out in cold glacial acetic acid solution, and the composition of the product determined by the method of thermal analysis with the aid of data derived from mixtures of substances of the types (A) and (B), which were prepared by appropriate alkylation of 4- and 5-nitroguaiacols, respectively. The directive powers found in this way were: MeO, 100; EtO, 135; $Pr^{\alpha}O$, 128; $Pr^{\beta}O$, 150; n-$C_4H_9{\cdot}O$, 123; $CH_2Ph{\cdot}O$, 113. It is interesting to note that Sonn and Patschke (*Ber.*, 1925, **58**, 1698) * have observed the order $CH_2{:}CH{\cdot}CH_2{\cdot}O > EtO > Pr^{\alpha}O > MeO$ for the orienting influence of these groups in the course of the preparation of ethers of β-resorcylaldehyde by the Gattermann synthesis.

Experimental.

Mixtures of 4-Nitro-2-ethoxyanisole and 5-Nitro-2-ethoxyanisole.—5-Nitroguaiacol was prepared by the method of Pollecoff and Robinson (J., 1918, **113**, 648) and in the nitration of 2-methoxyphenyl carbonate it was found advantageous to continue stirring at 0° for 3·5 hours. The ethylation of 5-nitroguaiacol was carried out by Ludwig's method (*Monatsh.*, 1900, **21**, 100) and also by the xylene–ethyl sulphate–potassium carbonate process. The yield was 65% and the m. p. 102°. 5-Nitro-2-ethoxyanisole (Freyss, *Bull. Soc. ind. Mulhouse*, 1901, **70**, 375), m. p. 85°, was similarly obtained in 60% yield from 4-nitroguaiacol. The freezing points were determined in a double-jacketed glass tube with the usual precautions. Nucleation and stirring were practised and the thermometer was graduated in fifths of a degree, but could be read accurately to the nearest 0·1°. As in all subsequent cases, the entire range of composition was examined and a portion of the curve selected for closer study either because the readings

* The work here described was carried out in 1922—1923 and the numerical results were disclosed when Part IV of this series was read at a meeting of the Society in June, 1925 (compare *J. Soc. Chem. Ind.*, 1925, **44**, 659T).

were more free from ambiguity in that region, or because the nitration mixture has a freezing point lying well inside the section.

The following data were employed in the present instance, the first number of each pair representing the percentage of 5-nitro-2-ethoxyanisole in the mixture: 31·5, 83·7°; 37·8, 79·5°; 42·4, 75·4°; 50·9, 66·3°; 54·1, 62·6°; 55·6, 60·1°.

Nitration of 2-Ethoxyanisole.—2-Ethoxyanisole, b. p. 213° (Tiemann and Koppe, *Ber.*, 1881, **14**, 2018) (10 g.) mixed with purified acetic acid (30 g.) was nitrated by the gradual addition of nitric acid (12·5 c.c.; *d* 1·42) in acetic acid (30 g.). The mixture was mechanically stirred and cooled in a freezing mixture; the highest temperature reached was 12°. After 45 minutes, the product crystallised and the temperature remained stationary at − 1°; water was then added, the solid collected, well washed and dried (yield 95%). The product (A) was crystallised from methyl alcohol (50 c.c.), and equilibrium ensured by keeping for 5 hours at 16°. The pale yellow crystals were collected, thoroughly drained under pressure, and dried (10·68 g.) (B). 7·1652 G. of (B) mixed with 0·5 g. of 4-nitro-2-ethoxyanisole froze at 66·0°. Hence from the graph, (B) contains 4·82 g. of 4-nitro-2-ethoxyanisole and 5·85 g. of 5-nitro-2-ethoxyanisole. In order to determine the composition of (A) it is necessary to estimate the solubilities of the isomerides in methyl alcohol at 16° and in presence of each other. 4-Nitro-2-ethoxyanisole (6·1860 g.) and 5-nitro-2-ethoxyanisole (3·8571 g.) were allowed to saturate methyl alcohol (25 c.c.) at 16°. The solid residue weighed 9·13 g. and its f. p. was 81·5°, corresponding to 34·9% of 5-nitro-2-ethoxyanisole. Combining these results, it appears that (A) contains 42·5% of 4-nitro-2-ethoxyanisole and 57·5% of 5-nitro-2-ethoxyanisole. That (B) contained the two isomerides only was shown by the fact that 7·1652 g. of (B) mixed with 1·0 g. of 4-nitro-2-ethoxyanisole froze at 68·9°. This corresponds to 51·4% of 4-nitro-2-ethoxyanisole, whereas the percentage calculated from the assumed composition of (B) is 51·9. This result and similar ones recorded below also guarantee the correct location of the points on the graph corresponding to the observed freezing points. The directive power of EtO relative to MeO (100) is therefore 135 in this series.

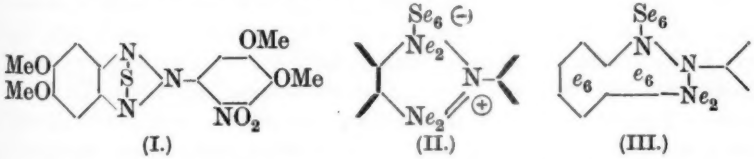
4 : 5-*Dinitro-2-ethoxyanisole.*—The mixture of mononitro-2-ethoxyanisoles was dissolved in cold nitric acid (*d* 1·42) and next day the product was precipitated by water and collected; it crystallised from alcohol in very pale yellow needles, m. p. 150° (yield almost quantitative) (Found: N, 11·6. $C_9H_{10}O_6N_2$ requires N, 11·6%). The m. p. of this methoxyethoxy-compound appears anomalous, since the related dimethoxy- and diethoxy-compounds melt at

132° and 113° respectively. By successive reduction with zinc dust in aqueous alcoholic hydrochloric acid solution, addition of sodium acetate and of a solution of phenanthraquinone in aqueous sodium bisulphite, and boiling, a flocculent, yellow precipitate of 3-*methoxy*-2-*ethoxyphenanthraphenazine* is obtained. Crystallised from xylene, the substance has m. p. 231°, gives a deep magenta solution in sulphuric acid, and fluoresces violet in benzene (Found: N, 8·2. $C_{23}H_{18}O_2N_2$ requires N, 7·9%).

6′-*Nitro*-3′ (or 4′)-*methoxy*-4′ (or 3′)-*ethoxyphenyl*-4 : 5-*thiotriazocatechol Methyl Ethyl Ether*.—Jones and Robinson (J., 1917, **111**, 910) obtained a compound, $C_{16}H_{16}O_6N_4S$, by the action of hydrogen sulphide on 4 : 5-dinitroveratrole in aqueous alcoholic ammonia. This substance was shown to be a nitro-derivative, reducible to a related diazotisable amine, and it was considered to be 6-nitroveratryl-4 : 5-thiotriazoveratrole (I).

We have applied the reaction under similar conditions to 4 : 5-dinitro-2-ethoxyanisole and have thus obtained a yellow compound which was crystallised by the addition of alcohol to its solution in nitrobenzene. The substance closely resembles nitroveratrylthiotriazoveratrole and appears to be homogeneous. The yellow, rectangular plates, m. p. 175°, are sparingly soluble in alcohol or ether and moderately readily soluble in benzene or chloroform (Found: C, 51·6; H, 4·4; S, 7·8. $C_{18}H_{20}O_6N_4S$ requires C, 51·4; H, 4·8; S, 7·6%).

In these substances the SN_3 group is associated with 24 valency electrons and on the electronic theory of valency a reasonable assumption regarding the constitution of the thiotriazo-nucleus is that it contains the bipolar ion (II), where each straight line in thin type represents two electrons.



(I.) (II.) (III.)

It is very probable, however, that the nucleus has aromatic character and this requires a contribution of four electrons from the SN_3 group towards an aromatic sextet, two more being derived by fusion with the benzene nucleus. By analogy with glyoxaline these four electrons should be derived from the nitrogen atom joined to sulphur and from the double bond joining the other nitrogen atoms, giving the expression (III). Here, the sulphur atom is favourably situated for the purpose of increasing its covalency with the nitrogen atom and thus neutralising both its

own electrical charge and that on the ring members. The formula (II) is derived from an *o*-thionitrosoazobenzene derivative by a process of internal addition precisely analogous to that assumed by Burkhardt and Lapworth (J., 1925, **127**, 1749) for the first stage of the reaction between nitrosobenzene and ethyl methylenemalonate. In the case we have discussed, the place of the unsaturated ester is taken by the thionitroso-group and the place of the nitroso-group by the azo-group.

4-*Nitro*-2-*propoxyanisole*, prismatic needles, m. p. 106° (Found: C, 56·6; H, 6·1. $C_{10}H_{13}O_4N$ requires C, 56·9; H, 6·2%) and 5-*nitro*-2-*propoxyanisole*, hexagonal tablets, m. p. 72° (Found: C, 56·9; H, 6·5%) were obtained in 70% and 65% yield, respectively, from 5-nitroguaiacol and 4-nitroguaiacol by the action of propyl iodide and potassium hydroxide in boiling alcoholic solution during 5—6 hours.

Mixtures of 4-nitro-2-propoxyanisole and 5-nitro-2-propoxyanisole had the following freezing points, the first number of each pair representing the percentage of 4-nitro-2-propoxyanisole in the mixture: 31·5, 55·5°; 34·2, 59·9°; 36·7, 63·5°; 41·0, 69·6°; 44·2, 73·4°; 50·5, 79·3°; 53·6, 82·4°; 57·0, 84·6°.

Nitration of 2-*Propoxyanisole*.—2-Propoxyanisole (10 g.), b. p. 220—225° (Cahours, *Compt. rend.*, 1877, **84**, 1195, gives 240—245°), dissolved in pure acetic acid (45 g.) was nitrated below 9° by the gradual addition with stirring of a mixture of nitric acid (15 c.c.; *d* 1·42) and acetic acid (35 g.). After one hour the product was precipitated by water, collected, washed and dried (A; 96% yield). This material was crystallised from 70 c.c. of 80% ethyl alcohol and after attaining equilibrium at 16° the solid was isolated (B) (10·79 g.). (B) froze at 75·2°, corresponding to 46·2% of 4-nitro-2-propoxyanisole. This was verified by adding 0·5213 g. of 4-nitro-2-propoxyanisole, when the f. p. was 77·6°, corresponding to 48·7% of 4-nitro-2-propoxyanisole (calc., 48·7%). A mixture of the isomerides (11·8861 g.), f. p. 78·5° (corresponding to 49·75% of 4-nitro-2-propoxyanisole) was allowed to reach equilibrium with 80% alcohol (40 c.c.) at 16°. The isolated solid froze at 80·0° (corresponding to 51·25% of 4-nitro-2-propoxyanisole) and the alcohol dissolved 0·5151 g. From these results it may be calculated that (A) contains 43·9% of 4-nitro-2-propoxyanisole and 56·1% of 5-nitro-2-propoxyanisole. The directive power of Pr^nO is, accordingly, 128.

4 : 5-*Dinitro*-2-*propoxyanisole*, obtained in theoretical yield from the mono-nitration product of 2-propoxyanisole by the action of nitric acid (*d* 1·42), crystallises from alcohol in needles, m. p. 143° (Found: C, 47·0; H, 5·0. $C_{10}H_{12}O_6N_2$ requires C, 46·9; H, 4·7%).

4-*Nitro*-2-iso*propoxyanisole*, pale yellow, prismatic needles, m. p. 83° (Found: C, 56·7; H, 6·1. $C_{10}H_{13}O_4N$ requires C, 56·9; H, 6·2%) and 5-*nitro*-2-iso*propoxyanisole*, yellow prisms, m. p. 53° (Found: C, 57·0; H, 6·3%), were obtained like the ethyl and propyl compounds previously described, but in this case the yields were only 30% and 15%, respectively. The freezing points of mixtures of the isomerides were the following, the first number of each pair giving the percentage of 5-nitro-2-*iso*propoxyanisole: 24·6, 69·7°; 30·4, 66·7°; 35, 63·7°; 39·5, 60·2°; 48·1, 53·8°.

Nitration of 2-iso*Propoxyanisole*.—Guaiacol was converted into its *iso*propyl ether by boiling in alcoholic solution with an equivalent of potassium hydroxide and *iso*propyl iodide. The yield of a colourless oil, b. p. 210—215°, was 90% (Found: C, 71·6, 71·6; H, 8·4, 8·2. $C_{10}H_{14}O_2$ requires C, 72·3; H, 8·4%). Somewhat low results in carbon estimations appear to be normal in the case of these ethers. Thus Cahours (*loc. cit.*) found C, 71·7 for 2-propoxyanisole. The nitration (of 8 g.) was carried out in the usual manner, giving a product (A) in 92% yield which was crystallised from 45 c.c. of 80% alcohol. After standing at 15°, the solids (B) were isolated (7·6978 g.). A mixture of 6·5663 g. of (B) with 2·4954 g. of 4-nitro-2-*iso*propoxyanisole froze at 57·0°, corresponding to 56·0% of 4-nitro-2-*iso*propoxyanisole. Hence (B) contains 39·3% of 4-nitro-2-*iso*propoxyanisole. A further 0·34 g. of 4-nitro-2-*iso*propoxyanisole was added and the f. p. was then 58·2°, corresponding to 57·8% (calc., 57·6%) of the 4-nitro-derivative. 60 C.c. of 80% alcohol dissolved 2·3089 g. of a mixture of 4-nitro-2-*iso*propoxyanisole (5·0 g.) and 5-nitro-2-*iso*propoxyanisole (4·641 g.) at 15° and the residue was isolated. 6·3365 G. of this product mixed with 4-nitro-2-*iso*propoxyanisole (1·1973 g.) had f. p. 61·3°, corresponding to 61·75% of the 4-nitro-derivative. From the above data it may be calculated that (A) contains 40·0% of 4-nitro-2-*iso*propoxyanisole and the directive power of Pr^sO is 150.

4 : 5-*Dinitro*-2-iso*propoxyanisole*, prepared from the mixture of mononitro-derivatives of 2-*iso*propoxyanisole in the usual manner, is much more readily soluble in alcohol than the propoxy-isomeride and crystallises in rectangular plates, m. p. 129° (Found: C, 46·8; H, 5·0. $C_{10}H_{12}O_6N_2$ requires C, 46·9; H, 4·7%).

4-*Nitro*-2-n-*butoxyanisole*, m. p. 74° (Found: C, 58·3; H, 7·0. $C_{11}H_{15}O_4N$ requires C, 58·7; H, 6·7%), and 5-*nitro*-2-n-*butoxyanisole*, pale yellow prisms, m. p. 56° (Found: N, 6·6. $C_{11}H_{15}O_4N$ requires N, 6·2%), were obtained in the usual manner in 60% and 55% yield, respectively. The freezing points of mixtures of the isomerides are the following, the first number of each pair indicating the percentage of 4-nitro-2-*n*-butoxyanisole: 25·5, 39·8°; 28·3,

37·5°; 33·2, 32·6°; 36·5, 30·4°; 39·6, 33·2°; 42·7, 35·3°; 45·1, 35·7°; 46·9, 35·5°; 50·7, 39·6°; 52·2, 41·8°; 53·8, 44·1°.* A compound, f. p. 35—36°, appears to be formed containing 44% of the 4-nitro-isomeride. The eutectic on the side of the 4-nitro-isomeride is near 35° and on the side of the 5-nitro-isomeride it is near 30°.

Nitration of 2-n-*Butoxyanisole.*—The *n*-butyl ether of guaiacol was obtained in almost quantitative yield in the usual manner. It is a colourless oil, b. p. 236—239° (Found: C, 72·8; H, 8·8. $C_{11}H_{16}O_2$ requires C, 73·3; H, 8·9%), and, on nitration in acetic acid below 12°, gave a mixture of mononitro-derivatives (A) in 96% yield. This material was dissolved in 65 c.c. of 80% alcohol and, on cooling, an oil separated and subsequently crystallised. After keeping at 16°, the product (B) was collected, well drained, and pressed, and finally dried at 95° during an hour. (B) (8·5006 g.) mixed with 4-nitro-2-*n*-butoxyanisole (0·3088 g.) froze at 37·3°, corresponding to a mixture containing 49·0% of the 4-nitro-isomeride. On adding 0·3054 g. of the 4-nitro-isomeride, the f. p. observed was 39·6°, corresponding to 50·7% of the 4-nitro-isomeride (calc., 50·7%). Further addition of 4-nitro-2-*n*-butoxyanisole (0·2977 g.) gave a mixture found to contain 52·1% of the 4-nitro-isomeride (calc., 52·2%). A mixture of 4-nitro-2-*n*-butoxyanisole (6·0833 g.) and 5-nitro-2-*n*-butoxyanisole (6·5902 g.) was crystallised from 80% alcohol (50 c.c.) and, after standing at 16°, the solid was isolated and found to weigh 11·2734 g. and to freeze at 38·5°, corresponding to 49·75% of the 4-nitro-isomeride.

From the above data it follows that (A) contains 44·8% of 4-nitro-2-*n*-butoxyanisole and 55·2% of the 5-nitro-isomeride. Consequently the directive power of *n*-C_4H_9·O is 123.

4 : 5-*Dinitro*-2-n-*butoxyanisole*, obtained by further nitration of the mixed mononitro-derivatives in excellent yield, crystallises from alcohol in faintly yellow needles, m. p. 97° (Found: C, 48·7; H, 4·9. $C_{11}H_{14}O_6N_2$ requires C, 48·9; H, 5·2%).

4-*Nitro*-2-*benzyloxyanisole* was obtained in 75% yield from 5-nitroguaiacol by the action of benzyl chloride and potassium hydroxide in boiling alcoholic solution. It crystallises from alcohol in one of two forms, m. p. 93° and m. p. 98° (Found in material, m. p. 93°: C, 64·7; H, 5·2, and in material, m. p. 98°: C, 64·7; H, 5·1. $C_{14}H_{13}O_4N$ requires C, 64·9; H, 5·0%).

5-*Nitro*-2-*benzyloxyanisole*, m. p. 82°, was similarly obtained from 4-nitroguaiacol in 55% yield (Found: C, 64·9; H, 5·0%). The

* In this case and also that of the benzyloxy-series, sharper and more consistent readings were obtained if, after thorough nucleation, stirring ceased when the cooling became very slow in the neighbourhood of the freezing point.

freezing points of mixtures of the isomerides were the following, the first number of each pair indicating the percentage of 5-nitro-2-benzyloxyanisole: 17·1, 85·0°; 23·7, 80·0°; 33·6, 72·9°; 37·2, 69·2°; 41·3, 65·2°; 46·0, 57·2°.

Nitration of 2-Benzyloxyanisole.—2-Benzyloxyanisole (9·766 g.) dissolved in acetic acid (65 c.c.) was nitrated by the gradual addition of a mixture of nitric acid (20 c.c.; *d* 1·42) and acetic acid (35 c.c.) with cooling in ice and stirring. The temperature rose momentarily to 18°, but quickly fell to 8°. After an hour, water was added and the product (A) collected, washed and dried (yield 98%). The material was crystallised from 80% alcohol (80 c.c.) at 16°, and the solid (B) completely freed from adherent mother-liquor and dried (11·1332 g.). A mixture of (B) (6·3452 g.) and 4-nitro-2-benzyloxyanisole (2·0015 g.) froze at 67·0° and therefore contained 39·5% of 5-nitro-2-benzyloxyanisole. On adding more 4-nitro-2-benzyloxyanisole (0·451 g.), the f. p. was 69·1°, corresponding to 37·3% of the 5-nitro-isomeride in the mixture (calc., 37·5%). Alcohol (50 c.c. of 80%) was saturated at 16° by the addition of 4-nitro-2-benzyloxyanisole (5·0 g.) and 4-nitro-2-benzylanisole (4·2528 g.). The solvent contained 0·3972 g. of the mixed isomerides, whilst the separated material had f. p. 59·5° and thus contained 44·8% of 5-nitro-2-benzyloxyanisole. From the above data it appears that (A) contained 53·0% of 5-nitro-2-benzyloxyanisole and 47·0% of the 4-nitro-isomeride and that the directive power of $CH_2Ph{\cdot}O$ is 113.

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L.—*The Relative Directive Powers of Groups of the Forms* RO *and* RR'N *in Aromatic Substitution. Part II. The Nitration of some 2-Benzyloxyanisoles substituted in the Benzyl Group.*

By ALBERT EDWARD OXFORD and ROBERT ROBINSON.

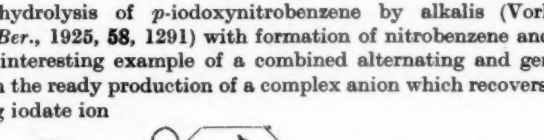
IN this communication the method described in the preceding paper is applied to the determination of the directive powers of the *m*- and *p*-nitrobenzyloxy- and *m*-methoxybenzyloxy-groups.

2-*m* (or *p*)-Nitrobenzyloxyanisole is much more difficult to

nitrate than is 2-benzyloxyanisole and it is evident that the introduction of the nitro-group has the effect of depressing the reactivity of the molecule as a whole. This effect is, however, felt to a greater relative extent by the benzyloxy-group than by the methoxyl. In Part I it is shown that the directive power of the benzyloxy-group (MeO, 100) is 113 and we now find that the *m*-nitrobenzyloxy- and *p*-nitrobenzyloxy-groups have, within the limits of experimental error, identical directive powers, namely, 67. Obviously the true value should be smaller still, because a portion of the inhibitory effect of the nitroxyl has been experienced by the methoxyl group. Since the nitro-group exerts its influence to an equal extent from the meta- and para-positions in the benzyl nucleus, it is not an alternating effect but, in all probability, a general polar effect which is under observation. The existence of general electrical effects is widely recognised, but it must be emphasised that, no less than in the case of the alternating effects, a knowledge of the mechanism of the reaction is necessary before a conclusion can be reached as to whether a particular process should be facilitated or hindered. An example will illustrate our meaning. Olivier (*Rec. trav. chim.*, 1922, **41**, 646) has shown that the hydrolysis of *o*-, *m*-, and *p*-nitrobenzyl chlorides in aqueous alcohol is much slower than that of benzyl chloride or any of its chloro-, bromo-, or methyl derivatives and this is another clear case of the general electrical effect of the nitro-group. The fact that the nitrophenols and nitrobenzoic acids, compared with phenol and benzoic acid, respectively, are strong acids shows that the nitro-group increases the affinity for the negative charge, whilst the weak basic nature of the nitroanilines, compared with aniline, shows that the introduction of a nitro-group decreases the affinity for the positive charge. An important exemplification of the latter point is found in the high chemical reactivity of nitro-substituted diazonium salts. Now, under the conditions of Olivier's experiments, the most acceptable view of the mechanism of the hydrolysis is that which postulates partial or complete dissociation of the nitrobenzyl chlorides at some stage and possibly as a result of oxonium salt formation with water or alcohol. Any such process will be inhibited if the affinity of the substituted benzyl group for the positive charge is diminished. Hence, on this mechanism, the theory of the general electrical effect of the nitro-group requires that the hydrolysis of a nitrobenzyl chloride should be slower than that of benzyl chloride. If, however, the benzyl chlorides were hydrolysed through the intermediate formation of a complex anion which subsequently recovered neutrality by ejecting chloridion, then the nitro-group, by increasing the affinity for the negative charge, would

facilitate the process.* Conversely, the introduction of nitro-groups into a molecule should retard the formation of complex kations such as those resulting from the attack of an aromatic compound by a diazonium ion, and this is in accordance with experience. It is a short step to the general case of aromatic substitution in which the nucleus is attacked by the positive end of a polarised complex rather than by a positive ion, and the same principles apply. If an aromatic nucleus, A, reacts with a complex, $\oplus$B–C$\ominus$, then the charge on B is transferred to the nucleus and the bipolar ion, $\oplus$A–B–C$\ominus$, is produced. Circumstances, such as the introduction of nitroxyl, which reduce the affinity of A for the positive charge must retard the process. In our experiments, the nitro-groups gave rise to no alternating effect whatever, but it should be noted that the system is a complex one summarised as: modifying group—activating centre—point of reaction. That is, the effect of the nitro-groups on the reacting nucleus is only experienced through an oxygen atom, which must be regarded as the effective key-atom. In Olivier's experiments very weak alternating effect (in the expected sense) is superposed on the powerful general effect, whilst Harrison (private communication) has shown that the hydration of 3 : 4′-dinitrotolane yields nothing but 3-nitrophenyl 4-nitrobenzyl ketone, (*m*-)$NO_2 \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot C_6H_4 \cdot NO_2$(*p*-), in accordance with the rule of alternate polarities. The general conclusion may be drawn that the alternating polar effect of a nitroxyl group cannot be discerned beyond the limits of the conjugated (crotonoid) system of which it forms a part. We had planned the determination of the directive powers of *m*- and *p*-methoxybenzyloxy-groups, but for reasons explained on p. 391 the latter estimation has not yet been made. The *m*-methoxybenzyloxy-group has the directive power 92 (MeO, 100; $CH_2Ph \cdot O$, 113) and it will suffice to note at this stage that the result is in harmony with the effect which a *m*-methoxy-group has in enhancing the ionisation constants of some substituted benzoic acids (*e.g.*, anisic acid, $K = 3{\cdot}2 \times 10^{-5}$; veratric acid, $K = 3{\cdot}8 \times 10^{-5}$).

* The hydrolysis of *p*-iodoxynitrobenzene by alkalis (Vorländer and Büchner, *Ber.*, 1925, **58**, 1291) with formation of nitrobenzene and an iodate is a most interesting example of a combined alternating and general effect resulting in the ready production of a complex anion which recovers neutrality by ejecting iodate ion



p-Dinitrobenzene does not undergo a similar reaction and this suggests that an important factor in the situation is the heavy iodine atom, which is doubtless capable of adding electrons to its outer shell.

EXPERIMENTAL.

2-m-*Nitrobenzyloxyanisole*, $OMe{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2$.—*m*-Nitrobenzyl bromide, m. p. 59—60°, was obtained in 96% yield by the action of bromine (32 g.) on a mixture of *m*-nitrobenzyl alcohol (31 g.) and red phosphorus (4 g.). A mixture of guaiacol (10 g.), *m*-nitrobenzyl bromide (17 g.), and alcoholic sodium ethoxide (430 c.c. of 0·5*N*) was refluxed for 1·5 hours, and the solid that was precipitated by addition of water was dried and crystallised from alcohol and then twice from light petroleum; it formed small, pale yellow needles, m. p. 47·5—48° (Found: C, 64·8; H, 5·0; N, 5·7. $C_{14}H_{13}O_4N$ requires C, 64·8; H, 5·1; N, 5·4%).

4-*Nitro*-2-m-*nitrobenzyloxyanisole*,

$$OMe{\cdot}C_6H_3(NO_2){\cdot}O{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2.$$

—The guaiacol carbonate process for the preparation of 5-nitroguaiacol, for some unascertained reason, gave very poor results in this series of experiments and we therefore obtained the substance by the nitration of acetylguaiacol and subsequent hydrolysis (Paul, *Ber.*, 1906, **39**, 2779). The ether of the nitroguaiacol was prepared by the method described for the *m*-nitrobenzylation of guaiacol, except that the reaction mixture was boiled for 2 hours. The substance was crystallised from acetic acid and then twice from alcohol, separating in almost colourless, microscopic plates, m. p. 164·5—165° (Found: C, 55·4; H, 4·3. $C_{14}H_{12}O_6N_2$ requires C, 55·3; H, 4·0%). All the *m*-nitrobenzyloxy-derivatives were more readily soluble in organic solvents than the corresponding *p*-nitrobenzyloxy-compounds.

5-*Nitro*-2-m-*nitrobenzyloxyanisole*.—The potassium salt of 4-nitroguaiacol which separates from the product of hydrolysis of 4-nitroveratrole (Pollecoff and Robinson, J., 1918, **113**, 645) proved to be homogeneous and was brought into reaction with an equivalent quantity of *m*-nitrobenzyl bromide in boiling alcoholic solution (400 c.c. for 12 g. of the salt) during 1·25 hours. The crude product, m. p. 140°, was twice recrystallised from alcohol, separating in colourless, microscopic plates, m. p. 140·5—141·5° (Found: C, 55·5; H, 4·2%).

Method of Determination of Freezing Points.—The material was placed in a thick-walled test-tube (8·5 × 1·5 cm.) provided with a standard Anschütz thermometer (graduated in fifths of a degree, but capable of being read accurately with the aid of a telescope to the nearest 0·05°) and a stirrer of stout silver wire. This vessel was surrounded by an air-jacket and the whole could be heated or cooled in a covered bath of sulphuric acid. The substances to be tested were finely powdered and dried for 10—12 hours at temperatures a few degrees below their m. p. About 1·3 g.

usually sufficed to cover the bulb of the thermometer. The temperature of the outer bath was kept at 20° above the m. p. of the material until this was completely fluid and thereafter at 2° below the f. p., which was ascertained in a rough preliminary experiment or by extrapolation. The liquid in the inner tube was slowly stirred until its temperature was 1·5—2° below the true f. p.; crystallisation was then induced by more vigorous stirring or by scratching; the temperature then rose to a maximum and remained at that temperature, the f. p., for 0·5—3 minutes, slow stirring being continued. In the neighbourhood of the eutectic, the degree of supercooling had a considerable effect on the observed f. p. and, on the other hand, as the mixture approached the eutectic it was less difficult to induce crystallisation. In every case several determinations of each f. p. were made and the mean of the most trustworthy values, the extreme variation not exceeding 0·3°, was calculated. It is not good practice to take the highest value and ignore the remainder, since this high value may have been obtained by some deviation from standard procedure.

Mixtures of 4-*Nitro*-2-m-*nitrobenzyloxyanisole and* 5-*Nitro*-2-m-*nitrobenzyloxyanisole.*

% 5-nitro-isomeride.	F. p.	% 5-nitro-isomeride.	F. p.
0·0	165·3°	50·2	137·0°
11·47	160·35	55·0	130·9
20·56	156·0	60·1	128·7
29·77	151·4	65·5	129·1 (?)
34·85	148·45	70·3	127·5
39·59	145·1	80·7	133·5
45·47	140·55	92·0	139·1
50·19	136·7	100·0	142·65
54·44	132·2		
Obtained by adding the 5-nitro-isomeride to the 4-nitro-isomeride.		Obtained by adding the 4-nitro-isomeride to the 5-nitro-isomeride.	

Nitration of 2-m-*Nitrobenzyloxyanisole.*—The ether (2·170 g.) dissolved in pure acetic acid (25 c.c.) was nitrated by the addition of boiled nitric acid (10 c.c.; *d* 1·42) in one portion, the mixture being mechanically stirred and efficiently cooled by water at 14°. Subsequent operations were exactly the same as those described below in the case of the *p*-nitrobenzyloxy-isomeride. The yield was 98·4% of that theoretically possible and in this case the correction applied to the f. p. was + 0·1°. The corrected f. p. of the nitration product (A) was 145·1° and from the graph this is found to correspond to 39·6% of the 5-nitro-isomeride (Lagrange interpolation formula—39·7%). The corrected f. p. of a mixture (B) of 1·2372 g. of (A) and 0·2520 g. of the 4-nitro-isomeride was 149·65°. From the graph this corresponds to 32·7% of the 5-nitro-isomeride (L.I.F.—32·9%) and hence (A) contained 39·4% (39·6%) of the

5-nitro-isomeride. The best value for the % of 5-nitro-2-*m*-nitrobenzyloxyanisole in the nitration product appears to be 39·6. Hence the directive power of the *m*-nitrobenzyloxy-group is 67. This was confirmed by taking 0·9579 g. of (B) and adding 0·2808 g. of the 5-nitro-isomeride, thus bringing the % of the latter to 48·1. From the graph, the f. p. should be 138·4° (Found: 138·2°).

Mixtures of 4-*Nitro*-2-p-*nitrobenzyloxyanisole and* 5-*Nitro*-2-p-*nitrobenzyloxyanisole.*—The compounds were obtained exactly like the isomerides and in excellent yields. They were crystallised thrice from benzene and obtained in pale yellow, flat needles, sparingly soluble in most organic solvents. The 4-nitro-isomeride has m. p. 167—168° (Found: C, 55·5; H, 4·0. $C_{14}H_{12}O_6N_2$ requires C, 55·3; H, 4·0%) and the 5-nitro-isomeride has m. p. 163·5—164·5° (Found: C, 55·3; H, 4·1%).

% 5-nitro-isomeride.	F. p.
0·0	168·3°
6·00	165·6
18·76	159·25
27·86	154·55
40·48	146·9
49·60	139·5

Obtained by adding the 5-nitro-isomeride to the 4-nitro-isomeride.

% 5-nitro-isomeride.	F. p.
49·4	139·3°
55·0	138·4
58·9	140·8
63·2	144·2
71·7	150·05
76·3	152·8
83·8	157·0
89·5	160·0
100·0	165·0

Obtained by adding the 4-nitro-isomeride to the 5-nitro-isomeride.

Nitration of 2-p-*Nitrobenzyloxyanisole.*—The *p*-nitrobenzyl ether of guaiacol was obtained like the *m*-nitrobenzyl ether and crystallised from alcohol in pale yellow, glistening leaflets, m. p. 63·5° (Found: C, 64·9; H, 5·0. $C_{14}H_{13}O_4N$ requires C, 64·8; H, 5·1%). The substance is readily soluble in ether, benzene, chloroform, or acetic acid, sparingly soluble in cold methyl or ethyl alcohol and in hot light petroleum. Lyman and Reid (*J. Amer. Chem. Soc.*, 1920, **42**, 615) quote the m. p. (63·6°) of the substance but give no further details. A solution of the ether (3·4 g.) in acetic acid (30 c.c.) was mechanically stirred, cooled in ice, and boiled nitric acid (3 c.c.; *d* 1·42) mixed with acetic acid (3 c.c.) was gradually introduced. After 2 hours, unchanged substance was recovered, whereas 2-benzyloxyanisole was readily nitrated under similar conditions. Next, the theoretical amount of nitric acid was added to an approximately 10% solution of the ether in acetic acid, and the mixture heated on the steam-bath to 90° without a colour change. One drop of nitric acid was then added and in a minute the liquid suddenly became red and in a short time a considerable amount of a yellow solid crystallised. The addition of a second molecular proportion of nitric acid produced no effect and the temperature

was then raised to 100° for 15 minutes, giving a clear solution. Water was added and the product collected, washed, and dried in the air and at 120° for 2 hours (Found: C, 55·2; H, 4·0. Calc.: C, 55·4; H, 4·0%). On analysis (f. p. 145·95°) this material was found to contain 42% of the 5-nitro-isomeride, and this conclusion was confirmed by addition of the 4-nitro-isomeride and the determination of the f. p. of the mixture.

Nitration at 14°. Boiled nitric acid (10 c.c.; *d* 1·42) was added to a stirred solution of the ether (2·422 g.) in acetic acid (30 c.c.) cooled by water at 14°. In about a minute crystallisation occurred without a change in the colour of the liquid, and after 15 minutes water was added and the product collected, washed, and dried at 80—100° for 10 hours. The yield was 99·1% of that theoretically possible. The f. p. of the crude product was 147·0° and in order to apply a correction for traces of impurities the following procedure was adopted. The finely powdered product (1·5 g.) was heated with pure methyl alcohol (10 c.c.) until the latter boiled; the mixture was then cooled, finally in water at 10°. The solid was collected, 10 c.c. of methyl alcohol being employed for washing the flask and an equal volume for washing on the filter. The material dried at 100° for 1 hour lost very little weight and had f. p. 147·2°. A repetition of the process gave a mixture, f. p. 147·0°. Hence the corrected f. p. of the nitration product is 147·4°. From the graph we find that the corresponding % of the 5-nitro-isomeride is 39·8 (L.I.F.—39·8). The corrected f. p. of a mixture of the nitration product (1·1706 g.) and the 4-nitro-isomeride (0·2419 g.) is 152·0° Using the interpolation formula, this corresponds to 32·5% of the 5-nitro-isomeride or 39·2% of the 5-nitro-isomeride in the nitration product. The best value for the composition of the mixture obtained by nitration of 2-*p*-nitrobenzyloxyanisole is 4-nitro-2-*p*-nitrobenzyloxyanisole 60·5% and 5-nitro-2-*p*-nitrobenzyloxyanisole 39·5%, whence the directive power of the *p*-nitrobenzyloxy-group is 67. On this assumption, the f. p. of a mixture of the nitration product (0·3842 g.) and the 5-nitro-isomeride (0·7388 g.) should be 154·5° on a branch of the curve not previously employed (Found: 154·25°). An artificial mixture of the two isomerides containing 39·5% of the 5-nitro-isomeride had f. p. 147·25° [Found: Nitration product, f. p. 147·0°; f. p. (corr.) 147·4°].

2-m-*Methoxybenzyloxyanisole*.—Guaiacol (4·9 g.) and *m*-methoxybenzyl bromide (8 g.) (Lapworth and Shoesmith, J., 1922, **121**, 1392) were added to a solution of sodium ethoxide (from 0·9 g. of sodium) in 95% alcohol (300 c.c.), and the mixture heated in the steam-bath for 10 minutes. The product was isolated by extraction

with ether after addition of water, and 4·0 g., b. p. 220°/22 mm., m. p. 28—31°, were obtained. By crystallisation from light petroleum the m. p. was raised to 31·5° (Found: C, 74·0; H, 6·5. $C_{15}H_{16}O_3$ requires C, 73·7; H, 6·6%).

4-*Nitro*-2-m-*methoxybenzyloxyanisole*, crystallising from alcohol in short, pale yellow, glistening needles, m. p. 116—117° (Found: C, 62·2; H, 5·4. $C_{15}H_{15}O_5N$ requires C, 62·3; H, 5·2%), and 5-*nitro*-2-m-*methoxybenzyloxyanisole*, crystallising from alcohol in very pale yellow, slender needles, m. p. 98·5—99·5° (Found: C, 61·8; H, 5·5%), were prepared by methods closely resembling those employed for the nitrobenzyl ethers of 5- and 4-nitroguaiacols. The yields were good.

Mixtures of 4-*Nitro*-2-m-*methoxybenzyloxyanisole and* 5-*Nitro*-2-m-*methoxybenzyloxyanisole*.—The following freezing points were observed, the first number of each pair indicating the percentage of the 5-nitro-isomeride in the mixture: 0·0, 114·85° (1); 11·78, 109·8° (2); 18·57, 106·8° (3); 21·52, 105·3° (4); 31·00, 100·35° (5); 34·20, 98·3° (6); 41·55, 93·1° (7); 50·20, 85·6° (8); 53·91, 82·5° (9); 62·23, 75·2° (10). In applying the Lagrange interpolation formula, the values (1), (2), and (3) were ignored, because in these cases supercooling to the extent of 3° or 4° was necessary. A smooth curve can be drawn through points corresponding to the values (1) to (9) inclusive, and (10) is probably on the other side of the eutectic.

Nitration of 2-m-*Methoxybenzyloxyanisole*.—The nitration was carried out like that of 2-*p*-nitrobenzyloxyanisole, except that the temperature was 0° and the flask was kept over-night in melting ice. The yield from 1·9642 g. of the ether was 2·3020 g. (99·0%) and the pale yellow, dry product had m. p. 78—94° (Found: C, 62·4; H, 5·3; N, 5·3. Calc.: C, 62·3; H, 5·2; N, 4·8%). The f. p. of the nitration product was 87·05°, whilst mixtures of the nitration product (1·6128 g.) with 0·2398 g. and 0·3608 g. of the 4-nitro-isomeride froze at 92·85° and 95·4°, respectively. Careful examination of these figures by graphical and algebraic methods, taking into consideration the fact that the f. p. 92·85° is close to a determined point (7) 93·1°, shows that the best value for the composition of the nitration mixture is 48·0% of 5-nitro-2-*m*-methoxybenzyloxyanisole and 52% of 4-nitro-2-*m*-methoxybenzyloxyanisole. The directive power of the *m*-methoxybenzyloxy-group is accordingly 92.

2-p-*Methoxybenzyloxyanisole*.—A solution of anisyl alcohol (5 c.c.) in benzene (30 c.c.) was saturated with hydrogen chloride. The reaction was very rapid. The solution decanted from the aqueous layer was dried by calcium chloride and, the excess of hydrogen

chloride having been removed in a current of dry air, added to a boiling solution of sodium ethoxide (from 1·0 g. of sodium) and guaiacol (6·5 g.) in absolute alcohol (300 c.c.); the mixture was then refluxed for 1·5 hours. The neutral ether, isolated in the usual manner, crystallised from light petroleum in rosettes of white needles, m. p. 94—96° (Found: C, 73·4; H, 6·5. $C_{15}H_{16}O_3$ requires C, 73·7; H, 6·6%). Despite repeated efforts, satisfactory conditions for the nitration of this compound could not be established. It has not, therefore, been possible to make use of the data recorded below.

4-*Nitro*-2-p-*methoxybenzyloxyanisole*.—This substance, prepared like the 5-nitro-isomeride described below, was crystallised from alcohol and then repeatedly from light petroleum, separating in very pale yellow, glistening needles, m. p. 129—130° (Found: N, 4·9. $C_{15}H_{15}O_5N$ requires N, 4·8%).

5-*Nitro*-2-p-*methoxybenzyloxyanisole*.—The *p*-methoxybenzylation of 4-nitroguaiacol was carried out in the usual manner, with *p*-methoxybenzyl bromide, but the yield was poor. After crystallisation from aqueous alcohol the substance melted at 108° with softening at 100°. Better results were obtained by the following method. Anisyl alcohol (4 c.c.) was converted into chloride in benzene solution as described above, and the liquid decanted from the aqueous layer shaken vigorously for one hour with a solution of the potassium salt (10 g.) of 4-nitroguaiacol in dilute aqueous sodium hydroxide (300 c.c.). The neutral product was extracted with ether, isolated, and crystallised from alcohol and then from light petroleum, separating in pale yellowish-brown, short needles, m. p. 109° with slight softening at 100° (Found: C, 62·2; H, 5·4. $C_{15}H_{15}O_5N$ requires C, 62·3; H, 5·2%).

Mixtures of the 4- and 5-nitro-2-*p*-methoxybenzyloxyanisoles had the following f. p., the first number of each pair indicating the percentage of the 4-nitro-isomeride: 0·0, 107·8°; 7·01, 103·7°; 19·14, 96·0°; 21·97, 93·4°; 23·20, 91·05°; 29·32, 85·75°; 38·11, 82·2°; 43·64, 91·05°. In this case, it was necessary to resort to seeding, as otherwise the degree of supercooling required was 3° or more.

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LI.—*The Relative Directive Powers of Groups of the Form* RO *and* RR'N *in Aromatic Substitution. Part III. The Nitration of some* p*-Alkyloxyanisoles.*

By ROBERT ROBINSON and JOHN CHARLES SMITH.

THE nitration of quinol dialkyl ethers in cold acetic acid solution results in an almost theoretical yield of the pure mononitro-derivatives and the composition of the product can therefore be determined with considerable accuracy by the method of thermal analysis. Satisfactory methods for the preparation of 2-nitro-4-methoxyphenol and 3-nitro-4-methoxyphenol and of the ethyl, propyl, and *p*-nitrobenzyl ethers of each of these substances have been devised and the f. p.'s of mixtures of the isomeric pairs of nitroquinol dialkyl ethers have been determined. Examination of the products of nitration of quinol methyl ethyl ether, quinol methyl propyl ether, and quinol methyl *p*-nitrobenzyl ether with the aid of the diagrams so obtained shows that the directive powers of ethoxyl and propoxyl relative to methoxyl are higher than those observed in the catechol series, whilst the *p*-nitrobenzyloxy-group is weaker in the quinol than in the catechol series. Furthermore, whereas propoxyl is weaker than ethoxyl in the catechol series, it is now found to be stronger than ethoxyl in the quinol series. The theoretical implications of these results are discussed in the following communication.

EXPERIMENTAL.

2-*Nitro*-4-*methoxyphenol*.—The product (90% yield) of the action of nitric acid (1 mol.; *d* 1·42) on quinol dimethyl ether dissolved in acetic acid at 30° had m. p. 71·5° and was homogeneous (Mühlhauser, *Annalen*, 1881, **207**, 253, gives 71·5°, and Vermeulen, *Rec. trav. chim.*, 1905, **25**, 12, gives 72—73°, as the m. p. of nitroquinol dimethyl ether). After reduction and attempted condensation with phenanthraquinone, no phenazine could be obtained and consequently 2 : 3-dinitroquinol dimethyl ether, one of the products of the further nitration of nitroquinol dimethyl ether (Nietzki and Pechberg, *Ber.*, 1890, **23**, 1211), was not present. The nitrations examined quantitatively in the course of this work were conducted at a lower temperature and it may be safely concluded that no dinitro-derivatives were produced. Under the following conditions, the hydrolysis of nitroquinol dimethyl ether gives a 96% yield of recrystallised 2-nitro-4-methoxyphenol (compare Kauffmann and Fritz, *Ber.*, 1910, **43**, 1215; Pollecoff and Robinson, J., 1918, **113**,

647). A mixture of nitroquinol dimethyl ether (40 g.), sodium hydroxide (80 g.), and water (700 g.) was refluxed in a copper flask heated in an oil-bath for 54 hours, the liquid being agitated by means of a moderately rapid stream of air. Water (400 c.c.) was then added, the condenser removed, and boiling continued for 30 minutes or until the issuing steam condensed to clear drops on a test-tube filled with cold water. The mixture was cooled to about 60°, acidified with hydrochloric acid, and distilled in a current of steam. The product was collected, dried, and crystallised from light petroleum, separating in red prisms, m. p. 79—80°.

2-Nitro-4-methoxyphenol is also the product of the hydrolysis of nitroquinol dimethyl ether by means of hydrobromic acid. Combined with the fact that nitroveratrole under similar conditions gives 5-nitroguaiacol (Cardwell and Robinson, J., 1915, **107**, 255), this indicates the order $o > m > p$ for the influence of a nitro-group on the ease of hydrolysis of methoxyl by acids. A mixture of nitroquinol dimethyl ether (5 g.) and saturated aqueous hydrobromic acid (15 g.) was heated on the steam-bath for 6 hours. Subsequently 2-nitro-4-methoxyphenol (3·0 g.), m. p. 72—74° (recrystallised, m. p. 79—80°), and nitroquinol (0·5 g.), m. p. 132°, were isolated and identified. The theory of the hydrolysis of methoxyl groups by acids is necessarily complex. In the Friedel-Crafts reaction with phenol ethers the order of influence of the carbonyl group on the ease of hydrolysis of methoxyl is $o > p > m$. On the other hand, in euxanthone diethyl ether, we find $m > o$, in harmony with the nitroveratrole case. In contrast, the hydrolysis of phenolic ethers by alkaline solutions, as affected by the positions of groups like nitroxyl, gives uniform results—o, $p > m$.

Quinol Monomethyl Ether.—The method of Ullmann (*Annalen*, 1903, **327**, 116) for the semi-methylation of quinol was found to give poor yields and the following process was adopted after numerous trials. A solution of quinol (110 g.) in sodium hydroxide (100 g.) and water (700 c.c.), contained in a flask filled with hydrogen, was cooled to 12° and vigorously shaken after the addition of neutral methyl sulphate (120 c.c.) in one portion. After about 5 minutes the mixture was cooled and the dimethyl ether collected (33 g., m. p. 56°). The filtrate and washings were acidified with hydrochloric acid and cooled to about 8° for about 1 hour, thereafter the monomethyl ether was collected, washed with ice water, and dried (45 g., m. p. 52—54°). The aqueous solution was extracted with ether and the residue after evaporation of the solvent yielded to benzene a further 30 g. of less pure quinol monomethyl ether, m. p. 41—46°. For our purposes, it was necessary to ensure the absence of quinol from the product. The material was dissolved

in benzene and any quinol which crystallised was separated; the solution was then distilled and a product, m. p. 53—54°, collected at 243—246°. This was redissolved in benzene, and the solution repeatedly shaken with small quantities of cold water. The ether was then again distilled, b. p. 243—244°, m. p. 56°. No coloration was developed in alkaline solution in contact with air. The substance crystallised from light petroleum has m. p. 56°, but when heated to about 200° and quickly cooled, the m. p. is 53°, changing in a week or two to 55°. Crystals, m. p. 56°, also change on keeping and the m. p. becomes 55°. Although these changes are small, the phenomenon is a real one.

Ethyl p-*Methoxyphenyl Carbonate.*—Ethyl chloroformate (95 c.c.) was added, with shaking and cooling in running water, to a solution of quinol monomethyl ether (124 g.) in water (300 c.c.) and sodium hydroxide (40 g.), and after 30 minutes the product was isolated by means of ether. The yield of a colourless, readily crystallising oil, b. p. 157°/17 mm., was 186 g. (93%). As traces of quinol monomethyl ether might have been produced in the distillation, the substance was washed with 0·05*N*-sodium hydroxide, dilute hydrochloric acid and water, and finally dried in a vacuum. The large, prismatic crystals had m. p. 21° (Found : C, 61·1; H, 6·2. $C_{10}H_{12}O_4$ requires C, 61·2; H, 6·2%). This ester is rather stable, 5 minutes' treatment with boiling 10% aqueous sodium hydroxide being necessary to effect complete solution.

Ethyl 3-*Nitro*-4-*methoxyphenyl Carbonate,*

$$OMe{\cdot}C_6H_3(NO_2){\cdot}O{\cdot}CO_2Et.$$

—Nitric acid (25 c.c.; *d* 1·52) was added to a solution of ethyl *p*-methoxyphenyl carbonate (25 g.) in acetic acid (25 c.c.), and the mixture heated on the steam-bath until the onset of a vigorous reaction manifested by the copious evolution of red fumes and a rise of temperature to 103°. After being maintained at 100° for 6 minutes, the liquid was cooled, water added, and the solid collected, washed, and dried (27·5 g. or 90%). The m. p. was 66°, and was raised only to 66·5° by crystallisation from light petroleum (Found : C, 49·7; H, 4·9; N, 5·9. $C_{10}H_{11}O_6N$ requires C, 49·8; H, 4·6; N, 5·8%). Slightly impure specimens are pale yellow and give a violet coloration with cold aqueous sodium hydroxide.

3-*Nitro*-4-*methoxyphenol.*—This substance, previously prepared by Klemenc (*Monatsh.*, 1914, **35**, 91) from its acetyl derivative, is best obtained in the following manner. A mixture of ethyl 3-nitro-4-methoxyphenyl carbonate (10 g.), sodium hydrogen carbonate (6 g.), methyl alcohol (17 c.c.), and water (17 c.c.) was boiled under reflux for 15 minutes, and the methyl alcohol then distilled from

the solution. The cooled, red liquid was acidified with hydrochloric acid; the yellow oil obtained quickly crystallised (6·7 g. or 95%). The m. p. was 97—99°, and 98—100° after crystallisation from benzene. The substance is dimorphous and when melted and suddenly cooled it solidifies to an orange mass which in a few seconds changes with a crackling sound to yellow needles. In one experiment the temperature rose to 99°. The phenomenon is readily observed in a capillary tube and the unstable modification appeared to melt at about 85°. The potassium salt of this nitrophenol immediately after drying is violet and readily soluble in acetone but, when kept for some days or ground in a mortar, it becomes crimson and sparingly soluble, even in boiling acetone. The whole point of the method adopted for the preparation of this substance resides in the avoidance of the use of powerful alkaline reagents in the hydrolysis, since the methoxyl in the *o*-position to the nitro-group is readily attacked, and even by hot sodium carbonate to an extent which would vitiate our results.

3-*Nitro*-4-*ethoxyanisole*.—2-Nitro-4-methoxyphenol (10 g.) was treated in alcoholic solution with potassium ethoxide (from 2·34 g. of potassium), and after the solvent had been evaporated the red potassium salt was dried at 130° in a vacuum for 2 hours. It was then mixed with absolute alcohol (50 c.c.) and ethyl iodide (9 c.c.) and heated in a pressure bottle at 100° for 3 hours. The alcohol was removed by distillation and the product washed with successive quantities of 1% aqueous sodium hydroxide and with water, collected and dried (10·3 g. or 86%). The crude product had m. p. 38—39° and after crystallisation from methyl alcohol and from light petroleum the substance was obtained in short, yellow prisms, m. p. 39·5° and f. p. 39·0° after drying in a vacuum at 100° for 1 hour (Found: C, 54·6; H, 5·7; N, 7·2. $C_9H_{11}O_4N$ requires C, 54·8; H, 5·6; N, 7·1%).

2-*Nitro*-4-*ethoxyanisole*.—A solution of potassium ethoxide (from 1·95 g. of potassium) in alcohol * (15 c.c.) was added to one of 3-nitro-4-methoxyphenol (8·45 g.) in alcohol (20 c.c.), and after the introduction of ethyl iodide (5 c.c.) the mixture was boiled under reflux for 1 hour; the original deep red colour had then given place to orange. The isolation was like that of the isomeride described above and there resulted 9·5 g. (95%) of yellow needles, m. p. 36—38·5°. The purest specimens had m. p. 37—39°, f. p. 38·4°, and were obtained by crystallisation from methyl alcohol and light petroleum (Found: C, 54·7; H, 5·8; N, 7·1%). When quickly cooled from

* In this case, the reaction is relatively facile and the use of ethyl alcohol is not disadvantageous. The ether was also prepared with methyl alcohol as the solvent.

100°, the substance melted sharply at 37°, but 1 hour later the m. p. was 37—39°.

Freezing Points of Mixtures of 3-*Nitro*-4-*ethoxyanisole and* 2-*Nitro*-4-*ethoxyanisole*.—Although these substances have a rapid rate of crystallisation, this is not the case with mixtures of them, especially near the eutectic, and the f. p.'s are ascertained only with great difficulty. In some examples the time taken to reach the maximum temperature after crystallisation had begun was no less than 20 minutes. Accurate standardisation of the procedure was therefore an urgent necessity. The external water-bath was contained in a Dewar vessel, and its temperature maintained 0·5° lower than that of the mixture. The mixture was supercooled 1·5°, nucleated from a trace of solid left on the thermometer stem, and stirred at the rate of 1 revolution per second. The temperature could be estimated to the nearest 0·02°. The eutectic could not be accurately located, since in this region a double f. p. was observed. The following mean values were selected, the first number of each pair indicating the percentage of 3-nitro-4-ethoxyanisole in the mixture: 0·0, 38·4°; 7·8, 34·7°; 18·2, 28·0°; 25·4, 24·35°; 31·6, 21·25°; 38·1, 17·5°; 40·75, 15·9°; 41·5, 14·15°; 43·1, 14·5°; 45·9, 12·1° (14·2°); 48·0, 11·8° (14·1°); 50·6, 13·9°; 57·6, 19·1°; 63·3, 22·3°; 67·8, 24·7°; 68·5, 25·2°; 75·7, 28·8°; 81·0, 31·1°; 84·3, 32·3°; 94·1, 36·3°; 100·0, 39·0°.

As a confirmation a mixture was made of 3-nitro-4-ethoxyanisole (1·0643 g.) and 2-nitro-4-ethoxyanisole (0·6413 g.) and found to freeze at 21·9°. From the graph, 21·9° corresponds to 62·4% of the 3-nitro-isomeride (calc., 62·4%).

Nitration of 4-*Ethoxyanisole*.—Fiala (*Monatsh.*, 1884, **5**, 233) has prepared 4-ethoxyanisole and states that its m. p. is 39°. Using pure quinol monomethyl ether and ethyl iodide, b. p. 72·4°, we find that the crystallised product has m. p. 36—37°, b. p. 216—217°/754 mm. (Found: C, 70·9; H, 8·0. Calc.: C, 71·0; H, 8·0%). The nitric acid employed in the nitrations described in this communication had *d* 1·42 and was distilled and freed from oxides of nitrogen by means of a current of air. The acetic acid also was purified and froze at 16°. A mixture of acetic acid (3 c.c.) and nitric acid (1·77 g.; 1 mol.) was gradually introduced by means of a capillary tube below the surface of a stirred solution of 4-ethoxyanisole (2·91 g.; 1 mol.) in acetic acid (6 c.c.) cooled to 4°. As no change of colour occurred, the temperature was allowed to rise to 6° after about 10% of the acid had been added. A yellow colour developed and the mixture was then cooled to 0—1° and the remainder of the nitric acid added during 20 minutes, after which stirring and cooling at 0° were maintained for 20 minutes. The temperature was then allowed

to reach 10° for 5 minutes. A further molecular proportion of nitric acid dissolved in acetic acid (1·5 c.c.) was introduced with similar precautions, and the mixture at 0° was then diluted with water (60 c.c.) at 2°. After being stirred for a few minutes, the mixture was kept for an hour. The oil had solidified and the clear supernatant liquid could be siphoned away without loss of the product. The material was then washed successively with water (20 c.c.) at 30°, twice with very weak aqueous sodium bicarbonate (10 c.c.) at 30°, and finally thrice with water at 30°. In each case stirring was resorted to and the washings were removed after solidification of the oil by cooling to about 5°. After drying to constant weight (3·565 g., 94·6%) in a vacuum, the specimen (*a*) was prepared for determination of the f. p. by heating in a vacuum at 100° for 30 minutes (Found: N, 7·2. Calc.: N, 7·1%). Further nitrations of 5 g. of 4-ethoxyanisole in an identical fashion gave 6·28 g. (*b*; 97%) and 6·23 g. (*c*; 96%) of the mixed isomerides.

The results of analysis are set out in the following table.

Specimen.	Grams of mixture taken.	Weight of 3-nitro-isomeride added.	F. p.	% of 3-nitro-isomeride indicated.	% of 3-nitro-isomeride in the nitration product.
(*a*) 1	2·6640	0	21·8°	62·2	62·2
2	—	1·4448	28·6	75·5	62·1
(*b*) 1	3·6087	0	21·95	62·4	62·4
2	—	1·5058	27·7	73·5	62·4
3	2·4048 of last mixture, f. p. 27·7°	2·2597	33·5	86·5	62·9
(*c*) 1	3·2733	0	21·9	62·4	62·4
2	—	0·9945	26·4	70·9	62·1
3	—	1·6532	28·4	75·0	62·4
					Mean 62·36

In order to ascertain what change of composition, if any, was entailed in the isolation processes, a mixture of the isomerides, f. p. 23·2°, was dissolved in the appropriate quantities of nitric and acetic acids so as to imitate the result of an actual nitration. Isolation and washing were carried out as described above, but before drying the whole series of operations was repeated. The dried material then froze at 23·4°. Two such treatments therefore only change the f. p. by 0·2° and if it is assumed that one isolation process raises the f. p. by 0·1°, the corrected composition of the product of nitration is 62·2% of the 3-nitro-isomeride and 37·8% of the 2-nitro-isomeride. Hence the directive power of ethoxyl relative to methoxyl (100) is 163 in the quinol series.

3-*Nitro*-4-*propoxyanisole*, $OMe{\cdot}C_6H_3(NO_2){\cdot}OPr^n$.—The propyl iodide employed in the preparation of this substance and of its isomeride had b. p. 101·2—101·7° (Found: I, 74·7, 74·7. Calc.:

I, 74·7%), and the propyl alcohol also was fractionated—b. p. 96·9—97·9°.

A mixture of 2-nitro-4-methoxyphenol (16·9 g.), potassium propoxide (from 3·85 g. of potassium), propyl iodide (20 c.c.), and propyl alcohol (50 c.c.) was boiled under reflux for 11 hours. The solvent was then removed in a vacuum at 100°, and the residue yielded to ether 10 g. (48%) of a dark brown liquid, m. p. 10·22°. This boiled at 127° under less than 1 mm. pressure and the clear yellow distillate had m. p. 10·35°. Repeated crystallisation from methyl alcohol at −15° raised the m. p. to the constant value of 10·7° (Found : C, 56·9; H, 6·4; N, 6·6. $C_{10}H_{13}O_4N$ requires C, 56·9; H, 6·2; N, 6·6%). In a second experiment, exactly the same results were obtained.

Attempts to improve the above process by employing the silver salt of the nitrophenol in place of the potassium salt were wholly unsuccessful. The silver salt of 2-nitro-4-methoxyphenol was prepared from the sodium salt and silver nitrate in aqueous solution. The material was dried in a vacuum (Found : Ag, 39·4. $C_7H_8O_4NAg$ requires Ag, 39·1%) and was remarkably stable towards alkyl iodides. Boiling methyl and ethyl iodides produced no effect in 10 minutes, and the action of boiling propyl iodide alone for 12 hours or in solution in ether, benzene, ethyl acetate, methyl, ethyl or propyl alcohol also gave negative results or very poor results.

2-*Nitro*-4-*propoxyanisole*.—This ether was obtained in 85% yield by the usual method applied to a methyl-alcoholic solution boiling during 12 hours. In all such processes the solvent chosen should be such that alcoholysis of alkyloxy-groups in the *o*- or *p*-positions to nitroxyl cannot introduce impurities. The pure substance, crystallised from methyl alcohol and from light petroleum, has f. p. 32·0° (31·98° in a second preparation) (Found : C, 57·0; H, 6·4; N, 6·7%).

Mixtures of 3-*Nitro*-4-*propoxyanisole and* 2-*Nitro*-4-*propoxyanisole*. —The following values of the f. p.'s were employed for the construction of a graph, and the first number of each pair indicates the percentage of 2-nitro-4-propoxyanisole in the mixture : 100·0, 32·0°; 95·9, 30·55°; 92·6, 29·5°; 86·5, 27·45°; 80·5, 25·1°; 74·9, 22·9°; 68·6, 20·2°; 63·7, 18·0°; 57·5, 15·0°; 53·1, 12·8°; 48·0, 10·35°. The readings for the mixtures containing less than 48% of the 2-nitro-isomeride were too indefinite to be of practical value.

Nitration of 4-*Propoxyanisole*.—4-Propoxyanisole (Fiala, *Monatsh.*, 1884, **5**, 234) was obtained in 85% yield in the usual manner and has b. p. 135°/15 mm. and m. p. 26—27°. The nitration was carried out in precisely the same way as that of 4-ethoxyanisole but, as the product was a liquid at 0°, it was necessary after the washings to await the complete settling of the droplets before removing the

supernatant fluid. The washed product was siphoned with the aid of methyl alcohol through a Pregl micro-filter into a weighed tube, and the methyl alcohol and water were removed by a current of filtered air at 50° and finally at 110° in a vacuum. In two experiments (*a*) and (*b*) the yields were 97% and 98%, respectively [Found in (*a*): N, 6·7. Calc.: N, 6·6%]. The results of the analysis are tabulated below.

Specimen.	Grams of nitration product.	Weight of 2-nitro-isomeride added.	F. p.	% of 2-nitro-isomeride indicated.	% of 3-nitro-isomeride in the nitration product.
(*a*) 1	1·1478	0·6043	15·1°	58·0	64·1
2	—	1·0971	19·5	67·1	64·3
3	—	1·6141	22·25	73·2	64·5
(*b*) 1	1·0771	0·6128	15·6	58·9	64·5
2	—	0·9326	18·85	65·6	64·2
3	—	1·2782	21·05	70·5	64·5
					Mean 64·35

As a check the following experiment was carried out. A mixture of 2-nitro-4-propoxyanisole (1·5173 g.) and 3-nitro-4-propoxyanisole (0·5560 g.) containing 73·2% of the former isomeride was made and this was found to have f. p. 22·25°, agreeing with the value read from the graph. This mixture (0·6 g.) added to that (*a* 3) of the same f. p. mentioned in the above table (1·0 g.) gave a product, f.p. 22·25°.

Corresponding to the above results, the directive power of the *n*-propoxy-group in the quinol series is 180.

3-*Nitro*-4-p-*nitrobenzyloxyanisole*.—2-Nitro-4-methoxyphenol (1·06 mols.), potassium propoxide (1·04 mols.), and *p*-nitrobenzyl bromide (1 mol.) were employed in the preparation of this substance in boiling propyl-alcoholic solution. The yield was 98% of the theoretical calculated on the *p*-nitrobenzyl bromide employed. The substance crystallises from benzene in yellow needles, m. p. 153°, f. p. 152·8° (Found: C, 55·3; H, 4·0; N, 9·2. $C_{14}H_{12}O_6N_2$ requires C, 55·2; H, 4·0; N, 9·2%).

2-*Nitro*-4-p-*nitrobenzyloxyanisole* was prepared in the usual manner in methyl-alcoholic solution and the yield was 96%. After recrystallisation from benzene, the substance was heated at 100° for an hour; it then melted at 120—125° with sudden evolution of benzene. After heating in a vacuum at 130—135° for 30 minutes in a slow current of air, the substance melted at 123·5° and froze at 123·0° (Found: C, 55·3; H, 4·3; N, 9·2%). The compound is more sparingly soluble in benzene than its less fusible isomeride.

Mixtures of 3-*Nitro*-4-p-*nitrobenzyloxyanisole and* 2-*Nitro*-4-p-*nitrobenzyloxyanisole*.—The outer bath of the cryometer was a large beaker of sulphuric acid. The following values of the f. p. were employed in the analysis below and the first number of each

pair represents the percentage of 2-nitro-4-*p*-nitrobenzyloxyanisole in the mixture: 100·0, 123·0°; 93·9, 120·25°; 87·9, 117·5°; 83·65, 115·65°; 78·2, 112·95°. The corresponding curve is almost a straight line. Nearer to the eutectic it was not found possible to obtain concordant readings, but the following mean values indicate the form of the curve: 74·25, 111·5°; 70·2, 109·9°; 67·6, 109·0°; 66·7, 108·4°; 59·8, 111·6°; 55·7, 114·4°; 49·4, 123·0°.

4-p-*Nitrobenzyloxyanisole.*—*p*-Methoxyphenol (1·05 mols.), potassium hydroxide (1·02 mols.), and *p*-nitrobenzyl bromide (1 mol.) in boiling methyl-alcoholic solution gave a 95% yield of the ether. The substance is sparingly soluble in cold methyl or ethyl alcohol, readily soluble in benzene, and crystallises from ethyl alcohol in large, yellow prisms, m. p. 87·5° (Found: C, 64·7; H, 5·1; N, 5·4. $C_{14}H_{13}O_4N$ requires C, 64·8; H, 5·1; N, 5·4%).

In view of the interest which has been evinced in regard to the bright yellow colour of nitroquinol dimethyl ether, it should be noted that this quinol methyl *p*-nitrobenzyl ether is more intensely coloured than either of the nitroquinol methyl *p*-nitrobenzyl ethers. This clearly indicates that the colour of nitroquinol dimethyl ether is due, not to any quinonoid rearrangement, but to the interaction of the *p*-dialkyloxybenzene nucleus and the nitroxyl functioning independently. The direct attachment of the nitro-group to the quinol nucleus depresses its reactivity and should have a bathochromic effect.

Nitration of 4-p-*Nitrobenzyloxyanisole.*—A mixture of acetic acid (12 c.c.) and nitric acid (12 c.c.; *d* 1·42) was added in one portion to a well-stirred solution of 4-*p*-nitrobenzyloxyanisole (3·0 g.) in acetic acid (30 c.c.). The temperature remained at 22° for 30 seconds, then rose to 25°, and the product began to crystallise. Water (150 c.c.) was added after 15 minutes, and the solid collected after 30 minutes and washed with water. The material (*a*) was dried at 80—90° for 10 hours and then weighed 3·45 g. (98%) (Found: N, 9·3. Calc.: N, 9·2%). A second specimen (*b*) was similarly obtained by nitration at 15—20° in 99% yield, and a third (*c*) by nitration at 16—21° in 99% yield.

Specimen.	Weight of nitration product.	Weight of 2-nitro-isomeride added.	F. p.	% of 2-nitro-isomeride indicated.	% of 2-nitro-isomeride in nitration product.
(*a*, *b*, *c*)	—	—	(109—110·5°)	—	(68—72·5)
(*a*)	0·7201	0·8143	117·2°	87·1	72·5
	—	1·4556	119·0	91·0	72·8
(*b*)	1·1561	0·9747	116·25	85·2	72·7
	—	1·7854	118·1	89·2	72·5
(*c*)	1·0287	0·8636	116·0	84·6	71·7
					Mean 72·4

A mixture of 2-nitro-4-*p*-nitrobenzyloxyanisole (0·9930 g.) and 3-nitro-4-*p*-nitrobenzyloxyanisole (0·1808 g.) contains 84·6% of the 2-nitro-isomeride and has f. p. 116·0°, confirming the graph in that region. When 1·17 g. of this mixture was added to 1·4 g. of the mixture (from *c*) given in the above table as of f. p. 116·0°, the f. p. was 116·0°. From the above data it appears that the directive power of the *p*-nitrobenzyloxy-group in the quinol series is 38.

An error of 0·1° in the f. p. causes an error of 0·2 in the percentage obtained from the graph and one of 0·4 in the calculated percentage composition of the mixture. In the case of ethoxyl an error of 0·1° in the f. p. produces an error of 0·27—0·3 in the calculated percentage composition of the nitration product, and in the case of propoxyl an error of 0·1° in the f. p. would cause an error of 0·24 in the percentage composition read from the graph and an error of 0·5 in the calculated percentage composition of the nitration product.

The authors wish to express their gratitude to the Royal Commissioners of the Exhibition of 1851 for a scholarship which enabled one of them to take part in the research, and also to the Chemical Society for a grant which has defrayed a part of the cost of the materials employed.

THE UNIVERSITY, MANCHESTER. [*Received, December 19th*, 1925.]

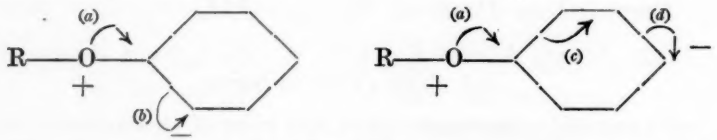
LII.—*The Relative Directive Powers of Groups of the Forms* RO *and* RR'N *in Aromatic Substitution. Part IV. A Discussion of the Observations Recorded in Parts I, II, and III.*

By JAMES ALLAN, ALBERT EDWARD OXFORD, ROBERT ROBINSON, and JOHN CHARLES SMITH.

IN order to avoid misconception as to the point of view adopted as a working hypothesis in this series of memoirs, a brief discussion of the fundamental principles is necessary.

It is recognised that certain ions, for example, those from sodium chloride, exhibit a high affinity for their charge and are relatively inert in the matter of co-valency formation, whereas other ions, for example, those from hydrogen cyanide or benzenediazonium hydroxide, have an intrinsic lower affinity for their charge and are active in the production of new bindings by co-valency. In effect, the former class are chemically inactive, the latter class active and, following Abegg and Bodländer, Kauffmann and Briggs, we can recognise in the two types diffuse and intense valency fields respec-

tively. Lapworth has recently contributed a valuable classification of reagents as *anionoid* or *kationoid* according as they behave in the same way as active negative or positive ions (Paper read at the Manchester Literary and Philosophical Society on March 3, 1925; see abstract, *Nature*, **115**, 625). Ethylene, butadiene and benzene are anionoid, their *active* free valency has a negative polar character, and it is obvious that the ethers and amines are even more definitely anionoid. The systems which one of us has called *crotenoid* (Robinson, *J. Soc. Chem. Ind.*, 1925, **44**, 456) are strongly anionoid, the natural character of the unsaturated carbon being reinforced by direct union with an *onium* element. Lapworth points out that, when ethylene polarises, the implication is that the unsaturated carbon with a positive charge is in the more natural or stable condition and is surrounded by a diffuse field. The active unsaturated carbon with a negative charge is in a less natural condition, and this is justly held to be related to the observation that, except C_2H,* no hydrocarbon radicals have been observed to occur with a negative charge in Thomson's vacuum tube experiments. Independent of these acute comparisons, the development of the theory of crotenoid systems (Decker, *Ber.*, 1905, **38**, 2893; Hamilton and Robinson, J., 1916, **109**, 1029; Robinson, *ibid.*, p. 1038; *Mem. Manchester Phil. Soc.*, 1920, **64**, 4; Robinson and Robinson, J., 1917, **111**, 958; 1918, **113**, 640; Kermack and Robinson, J., 1922, **121**, 427) required the assumption that the reactive carbon atoms in phenols and amines and their derivatives acquire a negative charge in the course of polarisation, the postulated precedent of all reactions. In the case of a phenol ether the mechanism of activation is represented by the annexed expressions.



The oxygen, by means of its free electrons, increases its co-valency with the ring C_α (process *a*). C_α recovers its normal co-valency by giving up correspondingly electrons to C_β (process *b*) (*o*-substitution) or by relinquishing $C_\alpha C_\beta$ co-valency electrons to $C_\beta C_\gamma$ (process *c*). C_γ must then relinquish $C_\gamma C_\delta$ co-valency electrons to the sole use of C_δ (process *d*) (*p*-substitution). In the activated form the oxygen is positively charged and is exhibiting oxonium character, a *rôle* in which it far more closely resembles, in its general stability, the satisfied ions ($\overset{-}{Cl}$, $\overset{+}{Na}$) than does the negatively charged

* As usual, a group derived from acetylene is exceptional.

carbon atom. The latter is intensely reactive and easily forms new co-valencies (compare *J. Soc. Chem. Ind., loc. cit.*, for the details of the mechanism of diazo-coupling on this hypothesis). This type of activation involves the displacement of electrons in a particular direction, *e.g.*, from left to right in the figures. Furthermore, since the oxygen acquires a smaller negative charge or an actual positive charge, the process must be the more facile the more highly negatively charged is the oxygen atom before the activation. This explains the descending order of reactivity in the series :

$$\overset{+}{\mathrm{Na}}\left\{\overset{-}{\mathrm{O}}\text{-}\langle\right., \quad \mathrm{MeO}\text{-}\langle, \quad \mathrm{O{=}CMe{-}O}\text{-}\langle\ ;$$

and in the series :

$$\mathrm{Me_2N}\text{-}\langle, \quad \mathrm{O{=}CMe{-}NH}\text{-}\langle, \quad \overset{-}{\mathrm{Br}}\left\{\mathrm{Me_3}\overset{+}{\mathrm{N}}\text{-}\langle\right..$$

In the acetoxy- and acetylamino-groups, conjugation gives the atom attached to the nucleus a positive charge (compare Rây and Robinson, J., 1925, **127**, 1618). It remains to add that the aromatic nucleus has a special stability of its own which Armit and Robinson (J., 1925, **127**, 1604) consider to be due to the possession of a stable electronic structure, the aromatic sextet. Electronic displacements are resisted by the sextet and it is a fact that the activation of a benzenoid centre in conjunction with any external group is feeble compared with that of an ethenoid complex in similar circumstances. Thus nuclear alkylation by the action of an alkyl halide on a crotenoid base occurs only with the more active aromatic systems. In the course of this investigation our views on the part played by the phenomenon of conjugation in organic chemistry have been more clearly focussed and it now appears possible to classify conjugated systems without arbitrary assumptions. Among the unit reactive groupings from which more complex structures may be derived, especial interest attaches to the highly unsaturated centres * typified by C=C, C=O (C≡N, N=O, etc.), and –O– (–NR–). Of these, C=O alone is kationoid. Certain groupings, C—R, to which definite conditions are attached, must be included. Combining the unsaturated groups two at a time in every possible way, we get :

(1) C=C—C=C; *butadienoid*; polarisation— $+|\overset{\curvearrowright}{\mathrm{C{=}C}}\mathrm{-}\overset{\curvearrowright}{\mathrm{C{=}C}}|-$; reactivity—anionoid.

Examples are isoprene, aromatic hydrocarbons.

* Certain special structures (ketens, acetylenes) are not considered and it is not suggested that the classification is a complete one.

(2) C=C—C=O; *crotonoid*; polarisation— $+|C{=}C{-}C{=}O|-$; reactivity—kationoid.

Examples are methylenemalonic ester, mesityl oxide.

(3) C=C—O—; *crotenoid*; polarisation— $-|C{=}C{-}O{-}|+$; reactivity—anionoid.

Examples are ethyl β-aminocrotonate, dimethylaniline, resorcinol.

(4) —O—C=O; neutralised system; polarisation—

$$+|{-}O{-}C{=}O|-;$$

reactivity—feebly kationoid at C and special characters (see below).

Examples are esters, amides, dianisylideneacetone.

(5) O=C—C=O, *quinonoid*, and (6) —O—O—, *peroxidic*, are heterogeneous systems which we do not propose to discuss.

Many more complex combinations of the unsaturated units are possible and especially it will be recognised that all the systems may be expanded by the inclusion of further C=C groups. In addition there are derived forms of which the following are the most important.

(7) O=C—C—X, where X is an atom or group independently capable of separating with a positive charge; *semi-crotonoid*; polarisation— $-|O{=}C{-}C{-}X|+$; reactivity—dissociation; often followed by rearrangement of the negative ion and anionoid character exhibited by the carbon atom previously joined to X. The process is analogous to the dissociation of a carboxylic acid.

Examples are acetone, 2 : 4-dinitrotoluene, ethyl α-bromoacetoacetate.

(8) C=C—C—Y, where Y is an atom or group independently capable of separating with a negative charge; *allyloid*; polarisation— $+|C{=}C{-}C{-}Y|-$; reactivity—kationoid.

Examples are phenyl allyl ether (Claisen and Tietze, *Ber.*, 1925, **58**, 275), geraniol.

(9) O—C—Y occurs in $MeO{\cdot}CH_2Cl$, etc.

The General Polar Effect.—Conjugation occurs by virtue of electronic displacements which produce an alternating polar effect* as

$$\overset{-}{A}\overset{+}{B}\overset{-}{C}\overset{+}{D}\overset{-}{E}$$

* An alternating polar effect in a chain ABCDE does not mean and never has meant either to Lapworth or to Robinson that the atoms are alternately positively and negatively charged. The phrase is taken to imply that evidence exists that in certain reactions, due to separate polarisations, A, C, or E may exhibit anionoid character and, on the other hand, one of the centres B or D may exhibit kationoid character. The alternation of

an inevitable consequence of the laws of valency operating in relation to changes in co-valency. Electronic displacements which do not involve co-valency changes require no alternation and may be continuous but diminishing in degree along a chain (compare Lapworth and Robinson, *Nature*, 1923, **112**, 722). Such displacements should occur in almost all types of molecules and will be propagated by electrostatic induction (Lewis, *J. Amer. Chem. Soc.*, 1916, **38**, 762; "Valence and Structure of Atoms and Molecules," pp. 84, 143; Thomson, *Phil. Mag.*, 1923, **46**, 497; Lowry, *Trans. Faraday Soc.*, 1923, **18**, 293; Lucas and Jameson, *J. Amer. Chem. Soc.*, 1924, **46**, 2475). We concur * with Lucas and Moyse (*ibid.*, 1925, **47**, 1459), for instance, in their application of the theory to the case of the addition of hydrogen bromide to Δ^2-pentene. The general effect of charged centres is obvious and Thomson (*loc. cit.*) has suggested both practical and theoretical methods of estimating the disposition of electrostatic doublets in various types of atomic combinations. In addition, the general effect of a group R can often be estimated by a consideration of the strength of the acid $R{\cdot}CO_2H$. All the evidence goes to show that hydrogen has a greater attraction for electrons than has the methyl group; we shall find it more convenient to express this statement in the converse form. This effect is represented, as in former cases (Malkin and Robinson, J., 1925, **127**, 370), by a straight arrow showing the direction in which the electrons are displaced. As an example of the interaction of the two types of electron displacement, we consider the carboxylic acids $R{\cdot}CO_2H$. The polarisation $O\overset{(b)}{=}C\overset{(a)}{-}OH$ proceeds until the positive charge† on the hydroxyl oxygen increases to such an extent that the proton is weakly held and can be removed by solvent molecules. The two oxygen atoms then divide the negative charge and assume identical functions. The displacement (*a*) is clearly the more fundamental process, but (*b*) is, however, a necessary

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stable and less stable octets was suggested by Kermack and Robinson (*loc. cit.*) as a possible, admittedly speculative, explanation of the tendency underlying the exhibition of this property. This suggestion was never intended to be regarded as a *mechanism* of activation, for which Kermack and Robinson retained an electronic translation of the theory of partial dissociation of conjugated complexes as developed by Robinson and Robinson (*loc. cit.*).

* Except, naturally, in considering that clear cases of the operation of continuous electron displacement dispose of the necessity for recognising the other type of displacement which occurs in conjugated systems.

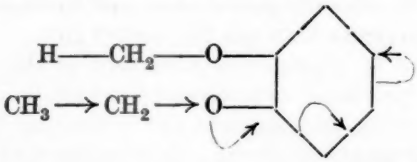
† Positive and negative are taken to mean also less negative and less positive respectively. Similarly, a smaller attraction is relatively a repulsion, and *vice versa*.

accessory in providing a means of adjustment of the disturbed co-valency of the carbon atom.

Contrasting $R \longrightarrow C\lessdot^{O}_{OH}$ and $R' \longleftarrow C\lessdot^{O}_{OH}$ it is apparent that the group R in repelling electrons *competes* with OH and to some extent inhibits the process (*a*), whilst the opposite is true of a group R′ which attracts electrons. Thus $R'\cdot CO_2H$ is a stronger acid than $R\cdot CO_2H$. The case of the phenols is simpler and again R′·OH should be a stronger acid than R·OH. Conjugation $R-\!\!-C(=O)-OH$ is also a factor, weakening an acid. This system does not exclude the consideration of the effect of a steric factor * (Flürscheim, J., 1909, **95**, 718) and is in excellent agreement with the available data.

The whole of the foregoing can be independently justified and we proceed to consider how these principles apply to the results recorded in the preceding communications.

In the ethyl ether of guaiacol we have the condition

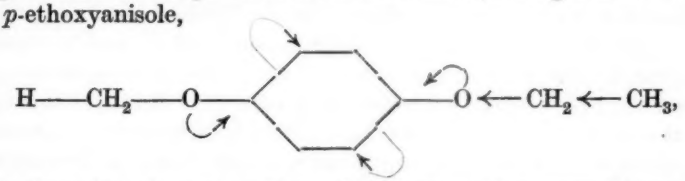


because the methyl group exercises a greater repulsion on electrons than hydrogen does. Therefore the polarisation of the crotenoid system, including the oxygen of the ethoxyl group, is facilitated as compared with the other system, not represented, which includes the oxygen of the methoxyl group. It follows that ethoxyl should have a higher directive power than methoxyl † (Found : EtO, 135; MeO, 100). The substitution of methyl for a second hydrogen atom should still further increase the directive power (Found : Pr$^{\beta}$O, 150). It is very interesting, however, that in the catechol series EtO, among *n*-alkyloxy-groups, appears to reach a maximum directive power (Found : EtO, 135; Pr$^{\alpha}$O, 128; *n*-C_4H_9·O, 123). This phenomenon we regard as due to the fact that as the chain lengthens a greater proportion of the general effect is distributed over the molecule and a smaller proportion, therefore, is effective through the attached atoms of the chain. Thus the ratio Directive

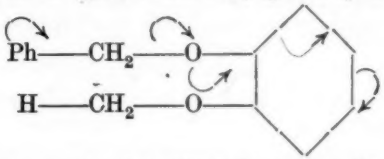
* Possibly also an electrical effect exercised across the intervening space rather than through the chain.

† The case of OH itself as against OMe cannot be considered on similar lines on account of the possibility of ionisation or removal of the proton from OH by the reagent.

power RO/Directive power MeO can be expressed as $y + a/x + a$,* where R is a higher alkyl group, y is its directive power apart from a; x is the directive power of methoxyl apart from a, a is a quantity depending on the general polar effect of the excess methylene groups in R — Me and is that portion of the effect which, owing to its distribution over the molecule, goes to assist the polarisation of the crotenoid system, including the oxygen of the methoxyl groups. As a increases, the ratio will approach some minimum value greater than 1. Our results can be interpreted on the assumption that the terminal methyl group of a *n*-propyl group exercises a general effect which is largely distributed over the molecule and only to a small extent transmitted through the attached chain. In the series of catechol experiments it is important to observe that the general effect must assist both conjugations, and the interest of parallel experiments in the quinol series is that this is no longer true. Thus in *p*-ethoxyanisole,



it is clear that the conjugations of the crotenoid systems themselves involve electronic displacements in opposing directions. The argument used in the catechol series still holds; ethoxyl should have a greater directive power than methoxyl, but if a portion of the general effect of the additional CH_2 of the ethoxyl is distributed, we can write: Directive power of EtO/Directive power of MeO = $y' + a'/x' - a'$. It might accordingly be anticipated that ethoxyl would have a higher relative directive power in the quinol than in the catechol series (Found: EtO in catechol series, 135; EtO in quinol series, 163). Furthermore, as a' increases, the value of the ratio $(y' + a')/(x' - a')$ must also increase, and the theory, which predicts a lower value for $Pr^{\alpha}O$ as compared with EtO in the catechol series, also requires in the quinol series that $Pr^{\alpha}O$ should be greater than EtO (Found: $Pr^{\alpha}O$ in quinol series, 180). In the benzyl ether of guaiacol we encounter one of the postulated conjugated systems (allyloid):



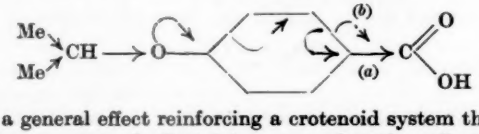
* The form of this expression is justified if x, y, a are taken as representing the number of occasions in unit time on which the different factors concerned lead to effectual polarisations.

In such a case the whole chain is not to be regarded as *one* conjugated system. The allyloid system * tends to assist the oxygen atom to acquire a negative charge, and this assists the related crotenoid system to function † (Found : $CH_2Ph{\cdot}O$, 113; MeO, 100).

In the *m*-methoxybenzyl group (directive power, 92), the methoxyl group has the general effect anticipated on the basis of Thomson's deductions concerning the situation of electrostatic doublets, and the whole group exercises less repulsion on electrons than the methyl group does. This is far more pronounced with *m*- and *p*-nitrobenzyloxy-groups (directive powers, 67). The identity of the directive powers of these two groups was unexpected and led us to adjust our views on conjugation in the direction now indicated. It must not, however, be hastily concluded that the nitro-group produces no alternating effect, even in these experiments, since the fact that *p*-nitrobenzoic acid is slightly stronger than the *m*-isomeride indicates a weak alternate effect. In the *m*-nitrobenzyloxy-group, we might have a slightly stronger general effect and a weaker alternating effect (crotonoid-type) than in the *p*-nitrobenzyloxy-group, and these small variations may balance. However this may be, the results show that if the nitro-group does produce an alternating effect it must be a very small one and this is normal because the reaction examined is one in which the substance exhibits anionoid character and conjugation of nitroxyl with the aromatic nucleus leads to the exhibition of kationoid properties. In the catechol series, for a group like the *p*-nitrobenzyloxy-group we have : Directive power of group/Directive power of MeO $= (z - b)/(x - b)$ and in the quinol series the ratio becomes $(z' - b')/(x' + b')$. Thus in the quinol series such a group should have a smaller relative directive power than in the catechol series (Found for the *p*-nitrobenzyloxy-group : in the catechol series, 67; in the quinol series, 38). In connexion with these deductions, it is important to notice that there

* It should be noted that the distribution of affinity in the butadienoid, crotenoid and allyloid systems on our electronic basis coincides with the requirements of Flürscheim's theory, but this is not the case in the crotonoid and semi-crotonoid types.

† The occurrence in some substances of quite complex combinations of general and alternate effects can be foreseen. Thus *p-iso*propoxybenzoic acid should be weaker than anisic acid or even than *p-n*-propoxybenzoic acid :



Here we have a general effect reinforcing a crotenoid system the polarisation of which produces a general effect (*a*), *or* a conjugation effect (*b*), or both; thereupon influencing the carboxyl as explained above.

are no side reactions to complicate the issue and that in all cases we have measured the whole effective directive power of the groups concerned. Consequently the small differences between x and x', y and y', and z and z' are not likely to affect the validity of our conclusions. We do not claim that the interpretation is more than an approximation to the truth.

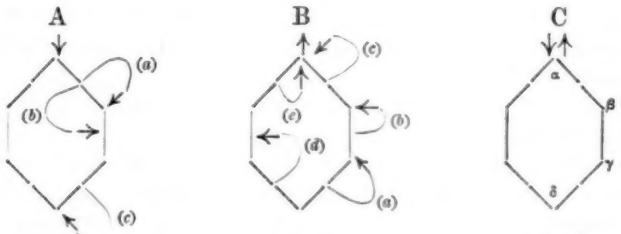
The point of view now adopted is one from which the general problem of orientation in aromatic substitution can be surveyed and we regard it as necessary to approach the subject in the following stages, which are of diminishing importance.

(1) Consideration of the circumstances of the reaction and especially whether the reagent is anionoid or kationoid.

(2) Consideration of the conjugated systems.

(3) Consideration of the general effect of attached groups on the conjugated systems.

We will confine ourselves to the cases such that there is no attached group conjugated with the nucleus and the reagent is kationoid (Br_2, HNO_3, etc.). In other words, we contemplate a normal benzenoid (butadienoid) system exhibiting anionoid character and wish to deduce from fundamental principles the nature of the effect of attached groups. In the case of a group, A, which repels electrons more than hydrogen does we have the arrangement (I). Here the crowding of electrons



Case I. Case II. Case III.

round C_α will facilitate, by repelling $C_\alpha C_\beta$ co-valency electrons, the polarisation of that particular butadienoid system which starts with C_α. The electron will be captured by C_β (process *a*; *o*-substitution) or, if not, a $C_\alpha C_\beta$ co-valency electron will become a $C_\beta C_\gamma$ co-valency electron (process *b*). C_γ, to recover its normal co-valency, must then correspondingly relinquish an electron to C_δ (process *c*; *p*-substitution). An alternative statement is that the ring carbon atom around which the density of electrons is greatest most easily becomes the positive end of a conjugated polarised complex. The applications will be obvious—toluene and *tert.*-butylbenzene are in the same category. In the case of a group B, which has a *strong*

attraction for electrons (II), it is easy to see in a general way that the circumstances are reversed, but in order to make the argument clear we take an extreme instance such that B has a definite positive charge. The electrical field emanating from B then produces positive electrification in diminishing degree over the portion of the molecule represented. One consequence is that all displacements of electrons in activation will tend to be towards B, and this inhibits para-substitution. Of all the remaining possible displacements (*a*, *b*, *c*, *d*, *e*), that indicated by (*a*) is the most likely to lead to reaction, because reaction depends on the acquirement of a negative charge and of all the carbon atoms which can be activated C_γ has the smallest positive charge. A less degree of electron displacement, therefore, will activate C_γ than will suffice for C_β. In order of preference we find in this case *m*-substitution, *o*-substitution, *p*-substitution, whilst displacement of the group B is also possible. An alternative statement is that the carbon atom (C_δ) furthest removed from the positive charge is least positive or most negative and most easily acquires a more positive charge and therefore most readily functions as the positively charged end of a polarised ethenoid or butadienoid complex. We cannot lay down any rules in regard to the required strength of the positive charge on B. The nitrogen of the nitro-group is positively charged if we accept the formulation $=\overset{|}{O}-\overset{|}{N}=\overset{|}{O}-$ in which each line represents an electron pair and it would appear that this group is effective even when separated from the nucleus by one carbon atom (Holleman, *Rec. trav. chim.*, 1895, **14**, 121).

Substitution in the *m*-position might also occur in a benzyl-ammonium ion.

The carbon atoms of the carboxyl, carbonyl and trichloromethyl groups can also be regarded as positively charged on the basis of independent evidence. This theory seems to harmonise better than any other which has been advanced with the facts of substitution in polycyclic aromatic groups, but a separate discussion of this subject is necessary. In the case of a group C (III) which in some phases attracts and in others repels electrons we anticipate predominating *o*-*p*-substitution because the phase in which electrons are repelled provides a favourable opportunity for activation leading to anionoid character, whereas the other phase in no way contributes to activation and in fact inhibits it.

In the case (I) a negative charge is distributed over the nucleus and anionoid character is intensified, leading to ready reaction, whilst in case (II) the distributed positive charge inhibits the exhibition of anionoid character. We can in fact estimate the

approximation of a group X to the types A or B by observing the ease of substitution of X–Ph as compared with that of benzene.

THE UNIVERSITY, MANCHESTER. [*Received, June 18th,* 1925.]

LIII.—*The Relative Directive Powers of Groups of the Form* RO *and* RR'N *in Aromatic Substitution. Part V. The Nitration of* p-*Methoxydiphenyl Ether.*

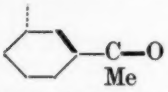
By THOMAS RUSSELL LEA and ROBERT ROBINSON.

THE three methoxydiphenyl ethers were prepared with the object of examining quantitatively the products of their fission by potassium, but the reaction proved to be a complex one and its study was deemed unlikely to furnish the desired information. In the course of our experiments, however, an observation was made which has a direct bearing on the subject of the present series. *p*-Methoxydiphenyl ether yields a single nitro-derivative (I) the constitution of which follows from its hydrolysis to *o*-nitro-*p*-phenoxyphenol (II).

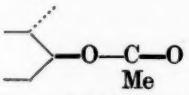
This proves that the directive powers of phenoxyl and *p*-methoxyphenoxyl are small compared with that of the methoxyl group and the result is in harmony with the theoretical conceptions outlined in the preceding memoir. The weak directive powers of the acyloxyl and phenoxyl groups are undoubtedly due to the same cause, namely, that the oxygen atom is conjugated on both sides.

Using the electrical conductivity analogy, the effect has been described as a "side tracking by a neighbouring system of high capacity" (*Chemistry and Industry*, 1925, **44**, 118). On Flürscheim's theory of alternating affinity demand, a similar explanation of the weakness of the phenoxyl group could be elaborated, but a consistent application of this hypothesis would appear to suggest that the acetoxyl group should have a strong directing influence. Yet *o*-methoxyphenyl acetate is nitrated exclusively in the para-position

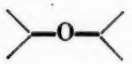
with respect to the methoxyl group. The following scheme illustrates this contrast :



Effect of COMe on nucleus.



Effect of COMe on O attached to nucleus.



Effect of Ph on O attached to nucleus.

EXPERIMENTAL.

m-*Methoxydiphenyl Ether*.—A mixture of *m*-methoxyphenol (15·5 g.), bromobenzene (15·5 g.), potassium hydroxide (6·2 g.), and copper bronze (0·1 g.) was heated under reflux (oil-bath at 240°) for 2·5 hours. The product was isolated by steam distillation, the excess of bromobenzene being first collected. The benzene extract of the distillate was washed with aqueous sodium hydroxide and water, dried, and distilled finally in a vacuum. The substance, b. p. 175°/20 mm., could not be crystallised (Found : C, 77·9; H, 6·2. $C_{13}H_{12}O_2$ requires C, 78·0; H, 6·0%). The yield was 19·0 g.

p-*Methoxydiphenyl Ether*.—This compound was prepared by the method described above for the resorcinol derivative and the yield was the same. The substance, b. p. 186°/32 mm., crystallised at −10°, but melted again at room temperature (Found : C, 77·8; H, 6·1%).

3-*Nitro*-4-*methoxydiphenyl Ether* (I).—A mixture of nitric acid (15 c.c.; *d* 1·42) and acetic acid (15 c.c.) was gradually added to a solution of *p*-methoxydiphenyl ether (5 g.) in acetic acid (20 c.c.) maintained at about 15° by cooling. Fifteen minutes after the addition of the nitric acid, water was added and the solid collected, washed, and dried (5·8 g.). The substance crystallised from alcohol in pale yellow prisms, m. p. 73—74° (Found : C, 63·7; H, 5·2. $C_{13}H_{11}O_4N$ requires C, 63·7; H, 4·9%). No other product of the reaction could be isolated. In a similar manner, *o*-methoxydiphenyl ether (Ullmann and Sponagel, *Ber.*, 1905, **38**, 2211) (5 g.) gave 4·9 g. of a solid product which crystallised from alcohol in long, colourless needles, m. p. 70—71° (Found : C, 63·5; H, 4·7%). In this case, however, only 2·8 g. crystallised from alcohol and an oil was precipitated by the addition of water to the alcoholic mother-liquor. It is probable that the product analysed is 3-*nitro*-6-*methoxydiphenyl ether*.

2-*Nitro*-4-*phenoxyphenol* (II).—3-Nitro-4-methoxydiphenyl ether (4 g.) was hydrolysed by a boiling solution of potassium hydroxide (30 g.) in water (200 c.c.) in a copper flask for 60 hours. The red solution with some red needles in suspension was acidified with hydrochloric acid and the yellow solid, which separated from an

emulsion, was collected, washed, and dried (1·0 g.). The substance crystallises from light petroleum in long, yellow needles, m. p. 51—52° (Found: C, 62·3; H, 4·0. $C_{12}H_9O_4N$ requires C, 62·4; H, 3·9%). The substance gives a bright red potassium salt and when boiled in xylene with potassium carbonate and methyl sulphate yields 3-nitro-4-methoxydiphenyl ether, m. p. 73—74°. Since Borsche (*Ber.*, 1923, **56**, [*B*], 1488) has shown that phenoxy groups in the *o*- or *p*-positions to nitro-groups are more reactive than similarly situated alkyloxy-groups, there can be no doubt in regard to the constitution of the product of nitration of *p*-methoxydiphenyl ether.

THE UNIVERSITY, MANCHESTER. [*Received, December 19th,* 1925.]

LIV.—*The Equilibrium between Methyl Formate and Methyl Alcohol, and Some Related Equilibria.*

By JENS ANTON CHRISTIANSEN.

THE announcement that the Badische Anilin- und Soda-Fabrik had succeeded in synthesising methyl alcohol from carbon monoxide and hydrogen attracted great interest. Patart (*J. Ind. Eng. Chem.*, 1925, **17**, 430, 859) claimed priority in this invention; but without entering into this discussion it may be mentioned that the process

$$CH_3{\cdot}O{\cdot}OCH + 2H_2 = 2CH_3{\cdot}OH \quad . \quad . \quad . \quad . \quad (1)$$

patented by the author in 1918, combined with the reaction

$$CH_3{\cdot}OH + CO = CH_3{\cdot}O{\cdot}OCH \quad . \quad . \quad . \quad . \quad (2)$$

investigated by Stähler (*Ber.*, 1914, **47**, 580), was the first which made it possible to prepare methyl alcohol from water gas, although any process by which the reaction

$$CO + 2H_2 = CH_3{\cdot}OH \quad . \quad . \quad . \quad . \quad . \quad (3)$$

can be carried out without methyl formate as an intermediate product must be of the greatest value.

The author was able to measure the equilibrium constant of reaction (1) by the kind permission of Prof. E. Biilmann, Director of this Laboratory, to whom he wishes to express his thanks. Later, in connexion with a firm in Copenhagen, Mr. Arne Olsen and the author made some measurements of the equilibrium constant of reaction (2). The results of these researches are in this paper: the substance of them was described, with the permission of the firm, in a lecture to the Chemical Society of Copenhagen on October 14, 1924.

Earlier work had shown that when methyl alcohol vapour is passed over reduced copper at 200° it splits up according to the equation

$$2CH_3{\cdot}OH = 2H_2 + CH_3{\cdot}O{\cdot}OCH \quad . \quad . \quad . \quad (-1)$$

and not, as stated by Sabatier, according to

$$CH_3{\cdot}OH = H_2 + CH_2O \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Before this result was published, Mannich and Geillmann (*Ber.*, 1916, **49**, 585) had drawn the same conclusion. As this reaction (−1) did not appear to be complete, a mixture of measured quantities of hydrogen and methyl formate was passed over reduced copper at about 180°, and a considerable decrease in volume observed, showing the occurrence of reaction (1).

To determine the equilibrium, a stream of electrolytic hydrogen, freed from oxygen by means of palladinised asbestos, and dried, was passed at a constant rate (by the use of a pressure regulator and capillary) through a saturator, containing methyl formate, in a thermostat. It then passed through a pipette containing reduced cuprous oxide on asbestos, which was heated in an electric oven, through two absorption tubes, and into a gas burette. The catalyst was reduced with hydrogen *in situ* before the experiment. The absorption tubes were filled with *N*/10-sodium hydroxide. In each experiment, the gas was allowed to escape before reaching the absorption tubes until the rate of flow and the temperatures of the saturator and the oven had been constant for some time. The escape was then stopped and the reaction products were collected. After a suitable time, the absorption tubes were removed and weighed (the hydrogen in them having been replaced by air free from carbon dioxide), and their contents titrated after addition of barium chloride (Winckler's method), so that both methyl alcohol and carbonic and formic acids were determined. The gas was analysed in an Orsat apparatus with platinum capillary. In this way, the amounts of methyl alcohol, methyl formate, hydrogen, carbon monoxide, and dioxide could be estimated. Allowance was made for water lost by evaporation from the absorption tubes, etc.

The equilibrium was also determined by starting with methyl alcohol. This was admitted directly to the catalyst in the oven from a burette through a capillary which was warmed above the b. p. of the alcohol. The results are in Table I, Nos. 1—10 being experiments on reaction (1), Nos. 11—17 on reaction (−1). The temperature of the oven was measured by a standardised thermometer placed outside the catalyst pipette; the error so produced was small, since the rate of flow was slow. The velocities in column 5 are in millimols. of methyl formate or pairs of millimols. of methyl

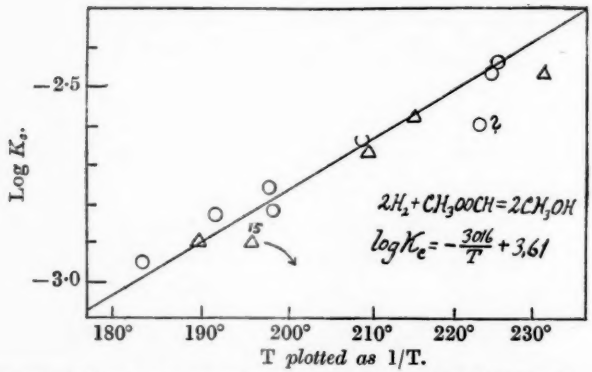
TABLE I.

No.	Temp. of oven.	Pressure in mm. Hg.	Temp. of water-bath.	Velocity. mmol./hr.	$CH_3 \cdot OH$. mmol.	$CH_3 \cdot O \cdot OCH$. mmol.	CO. mmol.	CO_2. mmol.	CH_4. mmol.	H_2. mmol.	$\frac{CH_3 \cdot O \cdot OCH}{H_2}$ v. p.	$\frac{CH_3 \cdot O \cdot OCH}{H_2}$ anal.	$K_1 \times 10^3$.
1	198·9°	758	13·56°	6·91	8·29	2·42	4·38	0·29		5·96	0·912	0·887	1·51
2	199·6	773	13·60	8·80	11·59	3·23	6·32	0·15	0·17	8·60	0·880	0·879	1·55
3	198·7	773	13·64	2·79	7·51	1·54	5·08	0·22	0·13	6·64	0·882	0·864	1·50
4	224·8	779	10·60	6·86	5·03	0·68	5·04	0·19	0·12	8·44	0·676	0·677	2·5
5	227·0	779	10·60	1·40	2·53	0·33	3·34	0·16	0·15	5·65	0·676	0·674	3·4
6	197·6	765	10·60	4·16	5·53	1·145	3·16	0·13	0·10	5·25	0·697	0·720	1·75
7	225·5	772	10·60	1·85	2·86	0·31	4·68	0·18	0·15	7·80	0·687	0·682	3·62
8	183·4	776	10·67	5·67	12·00	3·08	3·35	0·12	0·13	6·98	0·683	0·689	1·11
9	192·2	785	10·71	4·29	6·93	1·48	2·96	0·11	0·11	5·49	0·672	0·680	1·47
10	208·3	771	10·70	3·63	4·85	0·79	4·09	0·15	0·16	6·66	0·693	0·707	2·28
11	209·0	785		2·07	5·46	0·785	2·64	0·16	0·12	7·12	0·500	0·507	2·15
12	214·2	784		6·05	6·67	1·34	2·65	0·15	0·13	8·00	0·500	0·518	2·62
13	231·2	785		5·55	4·83	0·80	3·11	0·16	0·14	8·26	0·500	0·494	3·38
14	189·4	787		2·26	6·00	1·08	0·76	0·08	0·05	4·38	0·500	0·444	1·27
15	195·3	778		2·37	6·53	1·42	0·64	0·08	0·02	4·16	0·500	0·522	1·26
16	198·9	779		4·39	8·22	1·70	0·34	0·17	0·03	4·45	0·500	0·511	0·89
17	200·0	774		5·30	13·8	2·67	0·52	0·19	0·04	7·01	0·500	0·493	0·74

alcohol passing the catalyst per hour. Columns 12 and 13 give the initial ratio in molecules of ester to hydrogen, and are calculated (1) from the vapour pressure of the ester and the total pressure in the saturator, (2) from the analysis of the products; in the decomposition experiments the ratio should obviously be 0·500. These values give a check on the analyses, and show a satisfactory agreement. The values in the last column are those of the constant $K_1 = C^2_{H_2} C_{CH_3OOCH} / C^2_{CH_3 \cdot OH}$.

The values of $\log_{10} K_1$ (expts. 1—15) are plotted in Fig. 1 against $1/T$; they show that the results of association and dissociation experiments lie on the same curve, proving that true equilibrium was reached. The values of K_2 for the reaction $CH_3 \cdot O \cdot OCH = CO + CH_3 \cdot OH$ were so discordant as to show that equilibrium had not

FIG. 1.



△ (*dissociation*) *refers to experiments starting with* $CH_3 \cdot OH$ [*reaction* (−1)].
○ (*association*) „ „ „ „ „ $H_2 + CH_3 \cdot O \cdot OCH$ [*reaction* (1)].

been reached. The values obtained from expt. 15 (Fig. 1) and expts. 16 and 17 (not plotted) lie well below the curve; evidently the catalyst, which was the same in all these experiments, had lost its activity, so that even the equilibrium (±1) was not now attained.

The values for CO_2 and CH_4 in the table suggest that the reaction

$$CH_3 \cdot O \cdot OCH = CO_2 + CH_4 \quad . \quad . \quad . \quad . \quad (5)$$

took place to a slight extent. If, however, a trace of water was present, carbon dioxide may have been formed by the reaction

$$CH_3 \cdot OH + H_2O = CO_2 + 3H_2 \quad . \quad . \quad . \quad . \quad (6)$$

(*J. Amer. Chem. Soc.*, 1921, **43**, 1670); this would explain the excess of carbon dioxide found in some of the experiments.

The equilibrium constant of reaction (2) was determined in a

similar manner and in the same apparatus. The catalyst here was solid sodium methoxide. This absorbed some carbon monoxide, and hence the results are not very trustworthy. The same thing occurred, but to a much smaller extent (about 1 mol. of sodium methoxide disappearing for every 100 mols. of carbon monoxide converted into methyl formate), when the reaction was carried out in solution, and in this case the reaction causing the carbon monoxide to disappear was shown to be $CH_3{\cdot}O{\cdot}OCH + NaO{\cdot}CH_3 = CH_3{\cdot}O{\cdot}CH_3 + NaO{\cdot}OCH$. Hence the values of the equilibrium constant K_2 are only to be regarded as preliminary, but those of the association and dissociation experiments agree fairly well, as the following table shows.

TABLE II.

Reaction.	Temp.	Log K_2 by exper.	Log K_2 calc.
(−2)	102°	$\bar{1}$·82	$\bar{1}$·81
(2)	74	$\bar{1}$·53	$\bar{1}$·40
(−2)	74	$\bar{1}$·40	$\bar{1}$·40
(−2)	70	$\bar{1}$·29	$\bar{1}$·34

$K_2 = C_{CO} \cdot C_{CH_3{\cdot}OH}/C_{CH_3OOCH}$ is for the gas mixture leaving the catalyst. The values in column 4 are calculated by the equation $\log_{10} K_2 = -1880/T + 4{\cdot}82$.

The effect of temperature on equilibrium should be accurately given over a fairly wide range by an expression of the form

$$\log_{10} K = -A/T + B,$$

where A = heat of reaction at constant volume divided by 4·571, and B is a constant (Scheffer, *Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 636). Values calculated on this formula are in Table II and are represented by the straight line in Fig. 1. The values given in the literature for the heats of combustion of methyl alcohol and methyl formate are discordant, Stohmann's value for methyl alcohol being about 2 Cals. lower than that of Thomsen. I have preferred to use the latter, since, although Thomsen's " universal burner " is apt to give somewhat high values, the error may be expected to be small when the substances are volatile, whilst, on the other hand, Stohmann's values, according to Roth (*Z. Elektrochem.*, 1911, **17**, 789), may be suspected to be low, especially in the case of volatile liquids.

The heat capacity of methyl alcohol has been calculated from the values in Landolt-Börnstein's tables for the ratio, k, between the two heat capacities. For methyl formate, no direct data seem to be available, but from the value for ethyl formate and those for methyl and ethyl alcohols the heat capacity of methyl formate (at constant volume) has been estimated at 10 cals. per degree.

The following table contains all the numerical values used in the calculation of the reaction heats at the temperatures in question.

Substance.	Heat of combustion at const. press.	Heat capacity at const. vol.
Methyl alcohol	182,230	7·8
Methyl formate	241,210	10·0
Carbon monoxide	67,960	5·0
Hydrogen	68,430	4·8

By means of this table the heat of reaction (1) at constant volume and about 200° is calculated to be 13,800 cals. and that of reaction (2) at about 100°, 8,600 cals. From these values and the above determinations of the equilibrium constants, the constants, B, of reactions (1) and (2) can be calculated as 3·61 and 4·82, respectively. These two numbers thus contain the results of the above investigation of the two reactions.

It is now possible to obtain from Fig. 1 and Table II a preliminary value of the equilibrium constant $K_3 = C_{CO} \cdot C^2_{H_2}/C_{CH_3 \cdot OH}$ for the reaction (3). Calculation shows that

$$\log K_3 = -4896/T + 8{\cdot}43 \quad . \quad . \quad . \quad . \quad (7)$$

From (7) it can be calculated that at about 200° K_3 is about 10^{-2}, so that at this temperature, if the hydrogen concentration is 1 mol. per litre, only 1% of the carbon monoxide will remain if the reaction $2H_2 + CO = CH_3 \cdot OH$ proceeds until equilibrium has been reached, whilst, on the other hand, if the hydrogen concentration is 0·01, only 1% of the carbon monoxide will be transformed into methyl alcohol.

The value of K_3 can also be roughly predicted by means of one of the well-known approximate equations arrived at from Nernst's third law of thermodynamics, for instance, the one given by Nernst himself,

$$\log K_p = -Q_{18}/4{\cdot}57T + 3{\cdot}5 \log T + 2i_{H_2} + i_{CO} - i_{CH_3 \cdot OH} \quad (8)$$

where the i's are the so-called conventional chemical constants of the different molecular species.

As shown by Cederberg (*Dissert.*, Upsala, 1916), a close connexion seems to exist between the critical pressure of a substance and its chemical constant and therefore I have used the values $i_{H_2} = 1{\cdot}6$; $i_{CO} = i_{N_2} = 2{\cdot}6$; $i_{CH_3 \cdot OH} = i_{SO_2} = 3{\cdot}3$ (see Pollitzer, *Ahrens's Sammlung* **17**, 1912).

By means of $K_p = (RT)^2 K_c$ and the data just mentioned we thus find

$$\log K_3 = -22700/4{\cdot}57T + 1{\cdot}5 \log T + 4{\cdot}7 \quad . \quad . \quad (8, \text{i})$$

As furthermore 1·5 log T at temperatures about 200° is very nearly equal to 4·0, the equation becomes

$$\log K_3 = -4966/T + 8{\cdot}7 \quad . \quad . \quad . \quad . \quad (8, \text{ii})$$

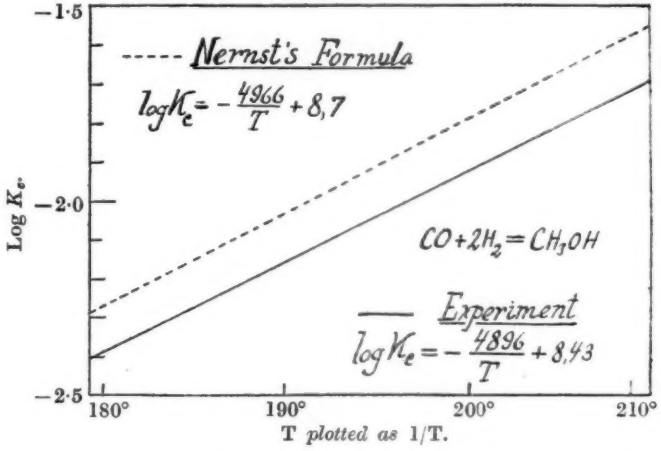
The agreement (see Fig. 2) between (8, ii) and (7) is as good as could be expected, considering the preliminary character of the investigation of reaction (2) and the approximations implied in the use of the Nernst equation (8).

By combining equation (7) with a similar relation derived from earlier experiments on the reaction

$$H_2O + CO = CO_2 + H_2 \quad . \quad . \quad . \quad . \quad . \quad (9)$$

it is furthermore possible to calculate the equilibrium constant of the reaction (6). If we define K_9 by means of the equation $K_9 = C_{H_2O} \cdot C_{CO}/C_{CO_2} \cdot C_{H_2}$, where the concentrations are those at equi-

FIG. 2.



librium, we get from Hahn's experiments (*Z. physikal. Chem.*, **1903**, **44**, 513; 1904, **48**, 735; see Haber, "Thermodynamik technischer Gasreaktionen," Berlin, 1905)

$$\log_{10} K_9 = -1854/T + 1{\cdot}66 \quad . \quad . \quad . \quad (10)$$

When this equation is subtracted from (8, ii) we obtain

$$\log_{10} K_6 = -3042/T + 6{\cdot}77 \quad . \quad . \quad . \quad (11)$$

where K_6 is the equilibrium value of $C_{CO_2} \cdot C^3_{H_2}/C_{CH_3 \cdot OH} \cdot C_{H_2O}$.

Finally it should be remarked that by means of existing data on the equilibria

$$C + 2H_2 = CH_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

and

$$C + CO_2 = 2CO \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

and the equations given above, it should also be possible to calculate the value of the equilibrium constant for the reaction (5).

The first of these reactions has been investigated by Mayer and

Altmayer (*Ber.*, 1907, **40**, 2134), Coward and Wilson (J., 1919, **115**, 1380), and Pring and Fairlie (J., 1912, **101**, 91). The results of these authors may be represented with sufficient accuracy by means of the equation

$$\log K_p = \log \frac{p_{CH_4}}{p^2_{H_2}} = \frac{5450}{T} - 6{\cdot}33 \quad . \quad . \quad . \quad (14)$$

If we wish to get $K_c = C_{CH_4}/C^2_{H_2}$ with the concentrations expressed in mols. per litre, we must add $\log RT = \log T - 1{\cdot}09$ and consequently

$$\log K_c = 5450/T + \log T - 7{\cdot}42 \quad . \quad . \quad . \quad (14, i)$$

For the reaction (14) a summary of the existing data is to be found in a paper by Jellinek and Diethelm (*Z. anorg. Chem.*, 1922, **124**, 220). From their table of the mean values of K_p found at different temperatures by different authors, the following expression may be calculated :

$$\log K_p = 8620/T - 8{\cdot}80 \quad . \quad . \quad . \quad . \quad (15)$$

and transforming into K_c,

$$\log K_c = \log \frac{C_{CO_2}}{C^2_{CO}} = \frac{8620}{T} + \log T - 9{\cdot}89 \quad . \quad . \quad (15, i)$$

By adding these equations we get the equilibrium constant for the reaction $2H_2 + 2CO = CH_4 + CO_2$, *viz.*,

$$\log K_p = \log \frac{p_{CH_4} \cdot p_{CO_2}}{p^2_{H_2} \cdot p^2_{CO}} = \frac{14070}{T} - 15{\cdot}13 \quad . \quad . \quad . \quad . \quad (16)$$

or $$\log K_c = \log \frac{C_{CH_4} \cdot C_{CO_2}}{C^2_{H_2} \cdot C^2_{CO}} = \frac{14070}{T} + 2 \log T - 17{\cdot}31 \quad (16, i)$$

Adding to this the equation (7), we get the logarithm of the equilibrium constant for the reaction $CH_3{\cdot}OH + CO = CH_4 + CO_2$, *viz.*,

$$\log K_c = \log \frac{C_{CH_4} \cdot C_{CO_2}}{C_{CH_3 \cdot OH} \cdot C_{CO}} = \frac{9170}{T} + 2 \log T - 8{\cdot}88 \quad . \quad . \quad (17)$$

from which it is evident that the formation of methyl alcohol from methane and carbon dioxide will take place only at temperatures at which methane is not at all stable, whilst it is possible, according to equations (11) and (7), to obtain reasonable amounts of methyl alcohol from hydrogen and either carbon monoxide or dioxide at not too high temperatures.

It is obvious that the equations given above all contain the uncertainty introduced by the use of the preliminary results for the equilibrium between carbon monoxide, methyl alcohol, and methyl formate.

Summary.

(1) The equilibrium constant of the reaction $CH_3 \cdot O \cdot OCH + 2H_2 = 2CH_3 \cdot OH$ has been determined with fair accuracy at temperatures in the neighbourhood of 200°.

(2) Preliminary values for the equilibrium constant of the reaction $CH_3 \cdot OH + CO = CH_3 \cdot O \cdot OCH$ at about 100° have been given.

(3) It is shown that by combination of the found values with existing data the equilibrium constants of the reactions $CO + 2H_2 = CH_3 \cdot OH$; $CO_2 + 3H_2 = CH_3 \cdot OH + H_2O$; and $CH_4 + CO_2 = CH_3 \cdot OH + CO$ may be calculated.

THE UNIVERSITY, COPENHAGEN. [*Received, September 21st*, 1925.]

LV.—*The Equilibria underlying the Soap-boiling Processes. The System Potassium Oleate–Potassium Chloride–Water.*

By JAMES WILLIAM MCBAIN and WILLIAM JOSEPH ELFORD.

THE study of soap solutions has shown that they exist in a number of forms, each with very striking characteristics. In pursuing the systematic study of the constitution of these liquids, jellies, liquid crystals, and curds, it is essential that the conditions under which each exists should be exactly delimited. Further, the processes of soap-boiling depend on the existence of this series of well-defined equilibria, which have, however, received very little systematic study.

We are now in a position to state that all soaps, pure, mixed commercial, whether potassium or sodium, are essentially of the same type. The differences are in degree and not in kind and the equilibria are so similar in the various cases that by means of numerical factors the effect of any electrolyte or mixture of electrolytes can be fairly closely predicted. Finally, to a large extent, the behaviour of a mixture of soaps can be inferred from that of its pure constituents taken separately. It is found also that the results from such small-scale laboratory experiments as are described in the present paper are in numerical agreement with similar results obtained on a full commercial scale.

Two previous contributions (McBain and Burnett, J., 1922, **121**, 1320; McBain and Langdon, J., 1925, **127**, 852) have dealt with the preliminary studies of sodium laurate and sodium palmitate in which the chief results were to show the various kinds of soap systems which exist, and to indicate some of the limits for the existence of ordinary isotropic soap solutions. The present instal-

ment is an account of a more thorough study of systems derived from potassium oleate,* which possesses the advantage of being so soluble that all the possible systems can be observed at room temperature. Further, application of the new methods of optical investigation that were developed in a previous study of potassium laurate have enabled progress to be made with the delimitation of the two important anisotropic liquids, neat soap and middle soap.

All these phases exist equally well in the absence of salt and the simplest procedure is to begin with the two-component system oleate and water, in which most of the typical equilibria appear. Accordingly, this will be discussed first, together with observations made upon individual phases, followed by the data obtained with systems in which potassium oleate is the third component.

Materials.—Kahlbaum's ordinary potassium oleate was found to be unsuitable, as it was not homogeneous and contained excess of acid and not only did the concentrated solutions on warming become dark reddish-brown but they sometimes differed in physical state from those of purer potassium oleate. Our preparations were therefore made by neutralising oleic acid "Kahlbaum" with potassium ethoxide and when carefully dried remained as white powders. The oleic acid in each case had a nearly correct iodine value and a molecular weight (by titration) about 1% too high (compare Laing and McBain, J., 1920, **117**, 1506). Potassium chloride "Kahlbaum" was used. Solutions were prepared in sealed thick-walled tubes of Duro glass by weighing in the requisite quantities and heating to whatever temperature was necessary to transform the contents into a single homogeneous liquid. Heating up to 170° was best carried out in a bath of glycerol, but for heating aqueous solutions to temperatures up to 400° an electric oven with mica windows was used and care was taken to heat and cool very slowly in order that adequate time should be allowed for the soap system to acquire the successive temperatures. Stirring was effected by slowly shaking the furnace as a whole, formation of air bubbles being avoided. In some cases a bath of the eutectic mixture of the nitrates of sodium and potassium was employed.

Methods of Observation.—In every soap system it is possible to observe a temperature, T_i, on heating to which it becomes a single homogeneous, isotropic liquid. For example, pure dry potassium oleate melts at 235—240° to form liquid crystal which, as will be shown, represents a point in the neat soap field, but on further

* A preliminary study was carried out by F. T. Maggs, who determined a number of points on the boundaries of the region of isotropic soap solutions.

heating to 300° this melts sharply to form an ordinary clear isotropic liquid. This liquid is miscible with water in all proportions; the more water present, in general the lower the temperature T_i, and at room temperature potassium oleate solutions up to $0{\cdot}7N_w$ are clear and isotropic.

All subsequent experience has confirmed the observations of McBain and Burnett (*loc. cit.*) that no supersaturation occurs, with respect to formation of anisotropic liquid, upon cooling the isotropic solution, but supersaturation readily occurs with respect to formation of either true lamellar crystals or crystalline curd fibres or needles. The sudden change in viscosity which occurs when anisotropic liquid appears, and the even more sudden change accompanying the completion of its formation upon cooling sufficiently, serve as useful although very rough checks upon the optical observations.

We have found it essential to use polarised light both for macroscopic and for microscopic observation. It is possible to examine a number of systems at room temperature and up to 80°, using an ordinary object slide and cover glass and a Guttmann heater (see Maclennan, *J. Soc. Chem. Ind.*, 1923, **42**, 393T), but it is essential that a truly representative sample should be taken and that the whole of the sample be examined. It is necessary also to ensure that the conditions observed in the calibration of the temperature scale be maintained throughout. When a mixture of isotropic and anisotropic soap solutions is thinly spread out and thus examined between crossed Nicols, the dark isotropic patches are seen to be sharply differentiated from the illuminated anisotropic portions of the field.

For work at higher temperatures no suitable substance could be found for sealing the cover glass to the object slide, as in some cases the properties of the soap were much affected by it as well as by evaporation. Professor Kenrick of Toronto University kindly supplied a cell, made by fusing together two optically ground plates of pyrex glass, with narrow side tubes sealed in, and such a cell has been used up to 120°. Latterly we have used small flattened glass cells made from tubing, 2·5 mm. in diameter, blown into a small bulb which during the process of blowing is squeezed flat between two hot carbon blocks, leaving room for only a thin film therein. The cell could be filled with a representative sample by suction and then sealed off. Such cells were very readily annealed, any optical evidence of strain being thus removed. They could be employed in a small electric furnace on the stand of the microscope, and the temperatures there observed agree closely with those obtained by a macroscopic study of large tubes.

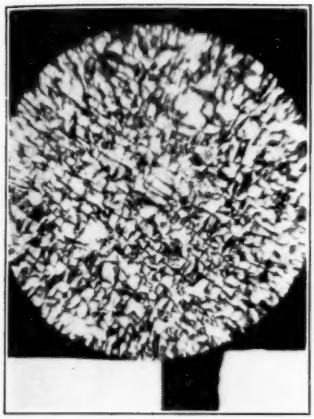
Equilibria in the System Water–Potassium Oleate.

Dilute aqueous potassium oleate is a homogeneous isotropic liquid which freezes with separation of ice, and at temperatures above 300° may without losing homogeneity be concentrated to 100% potassium oleate in the isotropic liquid condition. At all lower temperatures, potassium oleate is not miscible with water, but other intermediate phases are successively formed. Thus at 20° the highest concentration at which a homogeneous isotropic solution of potassium oleate can be prepared is $0{\cdot}70N_w$ (g.-mol. per 1000 g. of water). Above this concentration, an upper layer of higher concentration separates. This phase is a conic, anisotropic liquid and has been called in this laboratory "middle soap" (*Nature*, 1924, **113**, 534; **114**, 49; *Science*, 1925, **61**, 613; McBain and Langdon, *loc. cit.*). Middle soap exists over a limited range of concentrations as a homogeneous phase which constitutes, like the isotropic solutions, a colloidal electrolyte. There is no great difference in molar conductivity between soap in the middle soap phase and soap in the isotropic phase. Middle soap up to $1{\cdot}25N_w$ shows no structure in the cardiod ultramicroscope, but above this concentration diffuse granular patches begin to show against the dark background.

Middle soap exists over only a limited range of concentrations, above which another distinct phase of still more concentrated solution appears. To this phase we have extended the term "neat soap." Neat soap resembles middle soap in being a conic anisotropic liquid and in being plastic; that is, devoid of noticeable elasticity. Each is rigid, the neat soap much less so with about the consistency of vaselin. Middle soap is darker than neat soap (due to presence of impurity). A moderately thin specimen of middle soap is clear and transparent, whereas neat soap is better described as semi-transparent and somewhat turbid. The heterogeneous mixture of these two is rigid and turbid, the turbidity being at a maximum between the normalities $5N_w$ and $6N_w$. The exact range of concentrations for the existence of these phases has still to be determined, but for middle soap it lies between about $0{\cdot}9N_w$ and $3{\cdot}4N_w$ and for neat soap between $7{\cdot}5N_w$ and $12N_w$, within which limits a uniform field is obtained (see photograph I).

In many of the otherwise clear systems described above, small, white, star-like growths develop with time. Examination in the ultramicroscope shows them to consist of small rods plaited together to form branching structures. They probably consist of acid soaps produced by hydrolysis.

Photograph I, of $9N_w$-potassium oleate in polarised light, shows that neat soap, like middle soap, is a homogeneous, conic, anisotropic liquid soap with uniaxial interference figures. Further, on



I.—$9N_w$-Potassium oleate at room temperature. Crossed nicols. × 250.

II.—Concentrated aqueous potassium oleate. Crystal phase. Crossed nicols. × 250.

III.—$25N_w$-Potassium oleate at room temperature. Showing crystalline flakes and anisotropic fluid. Crossed nicols. × 60.

IV.—$13{\cdot}3N_w$-Potassium oleate at room temperature. Crystals as seen under cardiod ultramicroscope.

[*To face page* 424]

cooling $4N_w$-potassium oleate below its critical temperature, T_i 240°, the drops of neat soap which begin to appear separate in the form of the double cones which Lehmann (*Weid. Ann.*, 1895, **56**, 771, etc.) gave as a classical illustration of liquid crystals in systems containing ammonium oleate. Ethyl azoxybenzoate likewise separates in the form of these double cones when cooled from the isotropic, amorphous liquid condition. Friedel (*Ann. Physique*, 1922, **18**, 273) terms this structure " batomet " and regards it as proof that such systems are to be included in his so-called " smectic " group. Evidently both neat soap and middle soap are anisotropic liquids which would be included in the smectic group, and no soap systems are yet known which could be classified as " nematic." The fact that curd fibres have been shown by Mr. S. H. Piper to give radiograms with lines corresponding to spacings in three dimensions is a positive disproof of Friedel's contention that they were to be included in his " smectic " group, although he renamed the " liquides à conique " (conic anisotropic liquids) specially to include them.

At temperatures between 240° and 300° neat soap may be concentrated up to 100% anhydrous potassium oleate, but at lower temperatures there is an upper limit fixed by the separation of crystalline potassium oleate, usually in the form of extremely thin, hexagonal flakes. In the $50N_w$-solution there is still some neat soap left, showing that the hydration of the crystals cannot exceed 1 mol. of water per mol. of soap. It is not known whether these crystals of slightly hydrated potassium oleate can be dehydrated to anhydrous potassium oleate without any new phase separating. The excessively thin crystal plates are readily bent and are illustrated in photograph II.

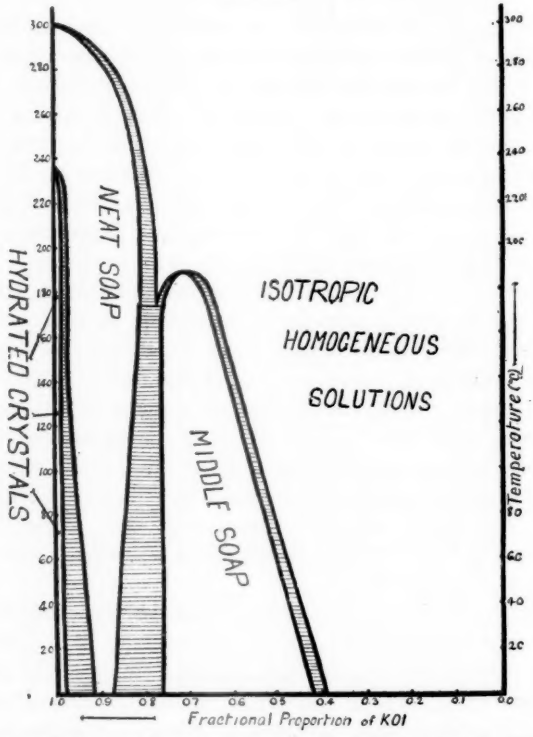
The sharply outlined hexagonal lamellæ are sometimes thin enough to give interference colours in ordinary light, and under a polarising microscope exhibit polarisation colours and give sharp uniform extinction in four positions. A mass of the crystals has a wax-like consistency and presents a silvery appearance. Photographs III and IV show these crystals mixed with neat soap in the heterogeneous systems.

Thus in passing from one pure component, water, to the other pure component, potassium oleate, at 20°, at least four different phases are met with and the solutions are alternately homogeneous and heterogeneous. At temperatures above 180°, the very remarkable behaviour is met with that there is a region of homogeneous isotropic phase above the middle soap as well as below it, so that, for example, at 177°, on steadily concentrating an isotropic solution the anisotropic middle soap separates, and after its formation is completed and the solution is slightly more concentrated, isotropic

solution of still higher concentration begins to appear but exists over a narrow range, whereupon neat soap appears.

All these relations are shown in Fig. 1 and some of the numerical data from which the figure has been plotted are in Tables IA, B, C and D. The temperatures there recorded are T_i, the minimum temperature at which the system is a homogeneous isotropic liquid,

FIG. 1.



Equilibrium diagram for the two-component system water–potassium oleate, showing the stable, homogeneous phases that occur at various temperatures. The boundary of the isotropic solution only is accurately known.

determined visually or with the aid of optical apparatus; T_h, the temperature on heating to which anisotropic plastic liquid shows, by a marked fall in rigidity, that isotropic liquid is beginning to separate; and T_c, the temperature on heating to which crystals just disappear to form homogeneous neat soap. Concentrations are expressed in weight normality (N_w), and also in "fractional proportions" of potassium oleate, $N_w/(N_w + 1)$, for use later in the triangular diagram of the three-component system.

Table Ia.

Appearance of aqueous potassium oleate at room temperature and phases present, together with temperatures, T_i, on heating to which the system becomes a clear homogeneous liquid.

Series a. *Tubes partly evacuated before sealing.**

System (N_w).	Fractional proportion of K oleate.	Description of material at room temp.	T_i (visual).
0·70	0·412	Viscous, colourless, isotropic liquid.	12°
0·72	0·419	Hetero. M. soap and isotropic liquid.	22
0·75	0·429	Hetero., etc., very viscous.	33
0·78	0·438	Clear, firm M. soap.	42
1·00	0·500	Clear, rigid M. soap, yellowish-brown.	72
1·50	0·600	" " " "	138
2·00	0·667	Clear, rigid, M. soap, deep colour.	185
2·50	0·714	" " " "	173
3·00	0·750	Hetero.†	175
3·50	0·778	Hetero.‡	184

Homo. = homogeneous. Hetero. = heterogeneous. M. soap = "middle soap." N. soap = "neat soap."

* The above systems were prepared from oleic acid of mol. wt. 285 and were all more deeply coloured than those prepared with 1924 (B) and 1925 soaps, possibly owing to a very slight amount of free oleic acid, which becomes oxidised at high temperatures. This would provide a possible explanation of the marked difference between $3{\cdot}5N_w$-solution prepared with this sample of soap and that prepared with succeeding samples.

† Minute droplets of a lemon-white phase in a brownish-red phase; system still rigid and plastic.

‡ Two immiscible plastic fluids, one lemon-coloured and tending to accumulate at the surface, the other deep reddish-brown and accumulating at the bottom of the tube.

Table Ib.

*Tubes not evacuated.**

System (N_w).	Fractional proportion of K oleate.	Description of material at room temp. (18—20°).	T_i (visual).
0·80	0·444	Hetero. M. soap and isotropic liquid.	34·5°
0·85	0·458	Homo. clear firm M. soap.	57
0·91	0·476	" " "	67
1·25	0·556	" " "	118
2·00	0·667	" " "	183·5
2·50	0·714	" " "	188
2·75	0·733	" " "	188·15
2·98	0·748	" " "	186
3·20	0·762	" " "	185
3·50	0·778†	" " "	200
4·00	0·800	Rigid, anisotropic, definitely turbid.	237·5

* Prepared from oleic acid of mol. wt. 286.

† Not quite as transparent as the $3{\cdot}2N_w$-solution.

Table Ic.

*Tubes not evacuated.**

System (N_w).	Fractional proportion of K oleate.	Description of material at room temp. (18—20°).	T_v (visual).	T_i (opt.).	T_e (visual).	T_h (opt.).
0·80	0·444	Viscous, hetero. M soap and isotropic liquid.	31·5°	32·5°.	—	—
1·00	0·500	Clear, rigid M. soap.	72	76	—	55°
1·50	0·600	,, ,, ,,	139	142·5	—	127
1·75	0·636	,, ,, ,,	161	173	—	163
2·00	0·667	,, ,, ,,	180	184	—	174
2·50	0·714	,, ,, ,,	188	—	—	—
2·75	0·733	,, ,, ,,	190	187·5	—	187
3·00	0·750	,, ,, ,,	185·5	—	—	—
3·10	0·756	,, ,, ,,	184·5	185·5	—	181
3·20	0·762	,, ,, ,,	183	—	—	—
3·28	0·766	,, ,, ,,	179·5	—	—	—
3·40	0·773	,, ,, ,,	178·5	—	—	—
3·50	0·778†	,, ,, ,,	194·5	200·5	—	173
4·00	0·800	Rigid, turbid N. soap and M. soap.	235·5	242	—	—
5·00	0·833	Hetero. rigid N. soap and M. soap.	261	—	—	—
6·00	0·857	Firm, hetero. N. soap and M. soap.	274·5	—	—	—
7·00	0·875	Semi-transparent N. soap.‡	283	—	—	—
8·00	0·889	Semi-transparent N. soap.§	280	—	—	—
9·00	0·900	Soft, semi-transparent N. soap.	287	—	—	—
10·00	—	,, ,, ,,	288·5	—	—	—
12·00	0·923	,, ,, ,,	291	—	26°	—
15·00	0·937	Hetero. N soap and cryst. flakes.	291·5	—	55	—
25·00	0·962	,, ,, ,,	293	—	98	—
30·00	0·968	,, ,, ,,	291	—	118	—
40·00	0·975	,, ,, ,,	303	—	132	—
50·00	0·980	,, ,, ,,	305	—	150	—

* Prepared from oleic acid of mol. wt. 286.

† Reproduction of 1924 (B).

‡ Turbidity subdued, and consistency less firm; can just be displaced by shaking.

§ Fluid, soft and non-homogeneous in appearance.

Table Id.

Systems prepared from pure aqueous potassium hydroxide and Kahlbaum's oleic acid, mol. wt. 285.

System (N_w).	Fractional proportion of K oleate.	Description of material at room temp. (18—20°).	T_i (visual).
1·15	0·535	Rigid M soap.	93·0°
1·24	0·552	,, ,,	115

Effect of the Presence of Potassium Chloride in Isotropic Solutions of Potassium Oleate.

Qualitative observations have been described by M. H. Fischer ("Soaps and Proteins," New York, 1921) on the effect of adding

salts to ordinary soap solutions. Some of his experiments were repeated by Miss King (*J. Soc. Chem. Ind.*, 1922, **41**, 147T). Fischer's observations were confined to fairly dilute soap solutions and were evidently influenced by the difficulties of ensuring adequate mixing and avoiding oxidation of soap, which greatly affect the results. The following observations were made by Miss King and F. T. Maggs as well as by ourselves.

The most important effect is that, whilst moderate additions of such salts as potassium chloride and potassium thiocyanate progressively increase the viscosity of the liquid, there is an ill-defined range of concentrations of salt for which the potassium oleate solutions set to a clear, transparent, elastic jelly like table jelly. For potassium chloride and potassium thiocyanate these concentrations are between about 0·4 and 0·8N_w. This range is somewhat wider if sufficient time is given for gelatinisation; the whole system remaining homogeneous and clear if hydrolysis and oxidation are avoided.

Still further small additions of salt reduce the jelly to a more or less viscous, homogeneous liquid. In solutions of such soaps as do not gelatinise under the given conditions, for example, sodium palmitate at 81°, the viscosity rises to a maximum and then falls off very greatly before any salting-out takes place (compare Miss King's graph, *loc. cit.*). Similar behaviour is observed within the whole range of isotropic solutions.

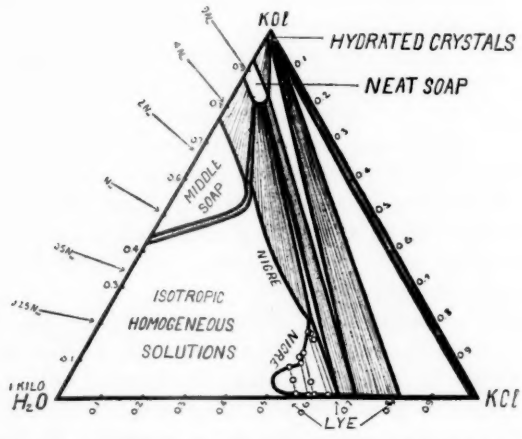
Still higher concentrations of salt cause separation of the soap solution into two layers. The concentration of salt necessary to effect this depends, in a rather complicated way, on the concentration of the soap, as is seen in Figs. 2, etc., in which the boundaries of the isotropic field are accurately mapped. If the solutions are sufficiently dilute, say below 0·6N_w-potassium oleate, the two liquid layers formed are both isotropic and are represented on the diagram within an indentation in the isotropic liquid boundary. The upper layer is "nigre" and contains most of the soap; the lower layer is "lye" containing a minute concentration of soap and a concentration of salt slightly higher than that in the nigre.

If the soap solution is more concentrated, say between 0·75N_w and 3N_w, the two phases separating out are neat soap and nigre. It will be noted that the presence of the salt greatly increases the possible concentration of soap in the isotropic solution; thus at 20° in the absence of salt the highest concentration at which potassium oleate forms a homogeneous isotropic liquid is 0·70N_w, whereas in the presence of 0·176N_w-potassium chloride the concentration of the soap may be increased to 3N_w. As in the two-component system, so in the three-component system, increasing temperature extends the boundaries of the isotropic field.

Equilibria in the System Water–Potassium Oleate–Potassium Chloride.

Middle soap and neat soap, like isotropic solution, extend from the two-component system, aqueous potassium oleate, into the three-component system; thus not only is the two-component system the limiting boundary of the three-component system, but the same phases occur in each and no new ones appear through addition of salt. Discussion of the three-component system is thus reduced to delimiting the boundaries for the existence of the phases, the appearance and properties of which have previously been dealt with. In other words, a reference to the foregoing discussion of

FIG. 2.



Phase rule diagram at 20°. Potassium oleate–potassium chloride–water; concentrations being expressed in fractions of mols. of potassium oleate and potassium chloride, but in fractions of one kilogram of water. The shaded areas represent the approximate direction of the tie lines in the two-layer systems.

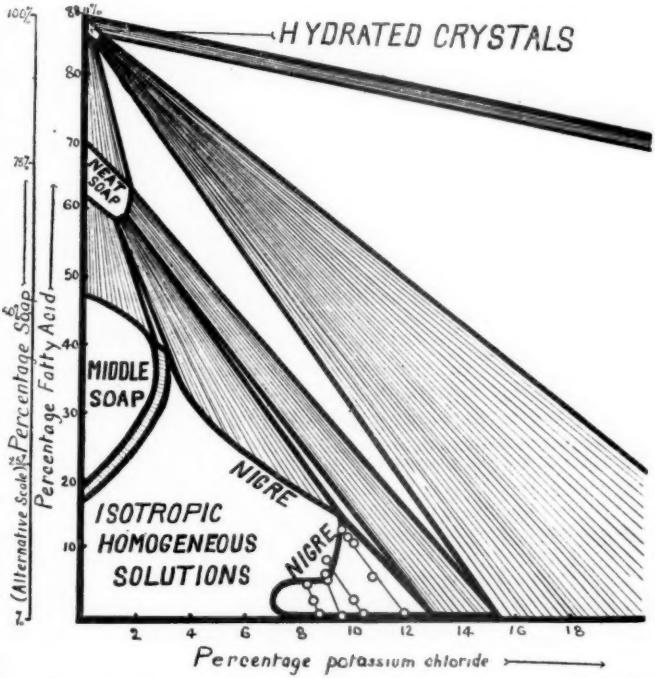
the two-component systems shows that solutions of pure soap spontaneously " salt out " in the absence of salt.

Most of the observations consisted in noting carefully the temperatures, T_i, at which heterogeneous systems just became isotropic, and it was found that these homogeneous isotropic solutions separated again at the same temperatures on cooling. It is only when the true crystalline lamallæ are due to appear that supersaturation has ever been observed.

Addition of salt to middle soap lowers the temperature, T_i, at which it becomes isotropic. Likewise, at higher temperatures, its field of existence progressively diminishes until at 189° it is reduced to a single point in the two-component system.

In most cases separation of the phases was so imperfect that they remained permanently in intimate mixture as a rigid, or extremely viscous mass, so that samples could not be separated for analysis. Indeed, the complete separation of neat soap from nigre, even in full-scale commercial work, is an art which calls for the highest skill on the part of the soap boiler, and middle soap has never been studied on the commercial scale. Apart from the extremely ready

FIG. 3.



Phase rule diagram at 20°, potassium oleate–potassium chloride–water; concentrations being expressed in grams of fatty anhydride and grams of potassium chloride per 100 grams of total system. The areas correspond to those in Fig. 2.

separation of lye from nigre, it has been considered impossible to effect separations in small-scale experiments. However, recent experience indicates that at high temperatures certain of these separations may be possible which will then permit of direct analyses of the separated layers.

The data are in Table II and the isotherms deduced therefrom are shown in Figs. 2 to 5, which should be compared with the corresponding diagrams for sodium palmitate (McBain and

Langdon, *loc. cit.*), where also a fuller introduction to the subject is given.

The five tie-lines between nigre and lye shown in Figs. 2 and 3, which illustrate the general equilibria at 20°, were obtained by direct analyses of the two phases in equilibrium with each other. The cross in the middle of each line represents the total composition of each system which should, of course, lie upon the straight line connecting the compositions of the two phases in each case.

TABLE II.

Effect of addition of potassium chloride to $0{\cdot}1N_w$*-potassium oleate; appearance and phases present at room temperature, and* T_1 *the temperature on heating to which the system becomes a clear homogeneous liquid.*

Conc. of KCl (N_w).	Description of material at room temp. (18°).	T_1 (visual).
0·00	Homo. transparent, isotropic liquid.	—
0·5	Isotropic, colourless, jelly-like system.	—
1·0	Moderately viscous, isotropic, opalescent liquid.	—
1·05	Two liquid layers; nigre and lye.*	25°
1·20	" " " " Both isotropic.	119
1·30	" " " " " "	127
1·50	" " " " " "	156
1·80	Two layers, upper hetero.	185
2·0	Two layers, N. soap and lye.	205

* Upper layer the more viscous, lower limpid lye, both isotropic.

Effect of addition to $0{\cdot}25N_w$*-solutions of potassium oleate.*

0·25	Colourless, limpid liquid, isotropic.	—
0·50	Clear, viscous liquid, isotropic.	—
1·00	Clear, very viscous, isotropic liquid.	—
1·25	Clear, isotropic, viscous liquid.	—
1·50	Two liquid layers, both isotropic.	100
1·65	" " " "	159
2·0	Two layers, upper hetero., lower lye	184
2·2	Two layers, upper viscous, lower lye.	204

Effect of addition to $0{\cdot}50N_w$*-solutions of potassium oleate.*

0·00	Clear, transparent, isotropic, mobile liquid.	—
0·25	Clear, isotropic, very viscous liquid.	—
0·50	Transparent, isotropic, elastic jelly.	—
1·00	Clear, viscous, isotropic liquid.	—
1·65	Two liquid layers, both isotropic.	75
1·67	" " " "	124
1·70	" " " "	120
1·80	Two layers, upper creamy, lower lye.	167
2·0	" " " " " Lye increasing.	178
2·3	Two layers, N. soap and lye.	207

Effect of addition to 0·75N_w-solutions of potassium oleate.

Conc. of KCl (N_w).	Description of material at room temp. (18°)	T_i (visual).
0·00	Hetero. M. soap and isotropic liquid.	33
0·1	Clear, elastic jelly, isotropic.*	—
0·25	Clear, transparent, elastic jelly, isotropic.*	—
0·50	Clear, transparent, rigid jelly, isotropic.	—
1·0	Clear, transparent jelly, isotropic.*	—
1·5	Clear, viscous, isotropic liquid.	—
1·7	Viscous hetero. system.†	25
1·75	Hetero.; bad separation.‡	109
1·85	Hetero., three liquid phases.§	150
2·0	Viscous, turbid upper layer. ‖	158
2·3	Turbid, aniso. upper layer and lye.	195
2·5	" " " "	206
2·75	" " " "	229·5

* Not perfectly rigid.

† Small amount of anisotropic phase at surface.

‡ Mainly clear, isotropic liquid of moderate viscosity; anisotropic phase near surface.

§ Middle nigre layer forms main bulk.

‖ Lye growing at expense of nigre.

Effect of addition to 1·0N_w-solutions of potassium oleate.

0·00	Aniso. plastic fluid, rigid.	72
0·085	" " "	65
0·10	Aniso. fluid, possessing elasticity.	60
0·17	Hetero. aniso. phase and isotropic jelly.	30
0·25	Clear, isotropic, transparent jelly.	—
0·50	" " " "	—
1·00	Clear, viscous, isotropic liquid.	—
1·50	Viscous hetero. system.*	65
1·6	Viscous hetero. system.*	104·5
1·75	Viscous hetero. system, aniso. phase and nigre.	130
2·0	Two layers, upper turbid, lower lye.	156
2·5	Two layers, upper turbid and viscous, lower lye.	193
2·8	" " " " " "	212·5

* Anisotropic phase tending to accumulate at the surface and viscous, isotropic liquid as lower layer; bad separation.

Effect of addition to 1·5N_w-solutions of potassium oleate.

0·00	Aniso. plastic fluid, rigid.	138
0·2	" " "	129·5
0·40	" " "	90
0·46	Clear, very viscous, isotropic liquid.	—
1·0	Hetero. system.*	60
1·35	Hetero., viscous, aniso. phase and nigre.	129
1·50	" " " " "	136
1·78	Two layers, upper hetero., lower lye.†	160
2·0	Two layers, upper turbid and viscous.	163
2·3	Two layers, upper turbid, lower lye.	191
2·5	Two layers, upper viscous and turbid, lower lye.	205

* Small amount of anisotropic phase near surface, mainly viscous, isotropic liquid.

† Upper layer forms main portion.

Note.—Only results obtained with systems prepared in non-evacuated tubes are recorded in this and the following sections, *i.e.*, results are those with 1924 (B) soap.

Effect of addition to 2·0N_w-solutions of potassium oleate.

0·00	Clear, aniso., plastic fluid, rigid.	183·5
0·1	Aniso., plastic fluid, rigid.	178·5
0·2	" " "	167
0·3	" " "	159
0·4	" " "	153
0·5	" " less rigid.	136
0·6	Aniso. plastic fluid.	91
0·7	Mainly clear, isotropic jelly.*	—
0·8	Clear, viscous, isotropic liquid.	—
1·0	Hetero.; bad separation.†	110·5
1·2	" " "	143
1·3	" " "	154
1·5	" " "	160
1·65	Two layers, upper viscous and turbid, lower lye.	183
2·0	" " " " " "	—
2·2	" " " " " "	—

* Little anisotropic phase near surface.

† Anisotropic phase and viscous, isotropic solution.

Effect of addition to 2·5N_w-solutions of potassium oleate.

0·0	Aniso. plastic fluid.	188
0·1	" " "	186
0·2	" " "	179
0·3	" " "	166
0·4	" " "	154
0·5	" " "	108
0·6	Heterogeneous.*	86
0·7	Heterogeneous.*	121
0·79 †	Hetero. aniso. phase and nigre; bad separation.	142
1·0	" " " " " "	163
1·3	" " " " " "	188
1·5	Three phases, lye just appearing.	197·5
1·65	Two layers, viscous turbid layer and lye.	215
3·5	" " " " "	247

* Anisotropic phase near surface, mainly clear, viscous nigre.

† 0·79N_w-KCl with 2·47N_w-K oleate.

Effect of addition to 2·75N_w-solutions of potassium oleate.

0·0	Aniso. plastic fluid, rigid.	188·5
0·2	" " "	170
0·25	" " "	164
0·30	" " "	158
0·40	" " "	144·8
0·50	Turbid, aniso., plastic fluid.	125
0·60	Hetero. aniso. phase and clear, viscous nigre.	150·5
0·80	" " " " "	175
1·0	" " " " "	184
1·65	Two layers, upper turbid and viscous, lower lye.	217

Effect of addition to $3{\cdot}0N_w$*-solutions of potassium oleate.*

Conc. of KCl (N_w).	Description of material at room temp. (18°).	T_i (visual).
0·0	Aniso. plastic fluid.	186
0·1	" " "	172
0·2	" " "	168
0·3	" " "	156
0·4	" " " Slight turbidity.	158
0·5	Viscous, semi-transparent system.	176
1·0	" " " "	208
2·19	Turbid fluid, upper layer and lye.	—
3·0	" " " "	237·5

Effect of addition to $3{\cdot}5N_w$*-solutions of potassium oleate.*

0·0	Aniso. plastic fluid.*	200
0·15	" " " Quite firm.	210·5
0·20	" " " " "	216·5
0·40	" " " " "	224·5
0·50	" " " " "	228·0

* Rigid but tending to turbidity.

Effect of addition to $4{\cdot}0N_w$*-solutions of potassium oleate.*

0·0	Rigid, aniso., plastic fluid.*	237·5
0·5	" " " " Turbid.	240
1·1	Two layers, neat soap and nigre.†	238

* Definitely turbid.

† Good separation of brown nigre, forming about ¼ of system.

Effect of addition to $5{\cdot}0N_w$*-solutions of potassium oleate.*

0·0	Very turbid, aniso., plastic fluid, rigid.	261
1·0	Two layers, N. soap and nigre.*	260

* Good separation of brown nigre, ¼ of system.

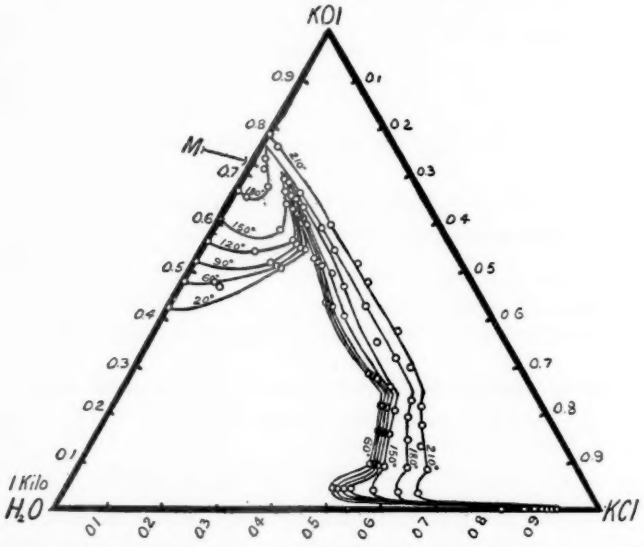
Fig. 2 represents the equilibria and the stable phases at 20°. It is the same equilateral triangle of unit height used in the previous papers, in which the respective corners represent 1 mol. of pure anhydrous potassium oleate, 1 mol. of potassium chloride, and 1 kilo. of water; and in which the co-ordinates are the fractions of these three quantities, the sum of which for each point on the diagram is unity. Although not so easily read as the rectangular diagram (Fig. 3), it is much more satisfactory for a complete survey of the field. In Fig. 3 technical units are employed for convenience of comparison with soap-boiling data.

Nearly half of each of Figs. 2 and 3 is occupied by the field of ordinary isotropic solutions. The general form of this extensive field resembles that for sodium palmitate (*loc. cit.*, Figs. 1 and 2), especially if the difference in temperature is taken into account. However, the greater solubility of potassium oleate is reflected in the distinctly larger amounts of salt which can be added without

destroying the homogeneity of the solution. The field of middle soap, though in both cases only approximately delimited, is much more prominent with potassium oleate, whereas the neat soap fields, as far as known, are fairly similar. The field representing crystalline soap is confined to a small part of the uppermost corner of the diagram on account of the low degree of hydration of crystals of potassium oleate. This field likewise requires further study.

In the previous communication (*loc. cit.*, p. 858) the possibility of the existence of a three-phase system, *viz.*, neat soap, nigre and

FIG. 4.



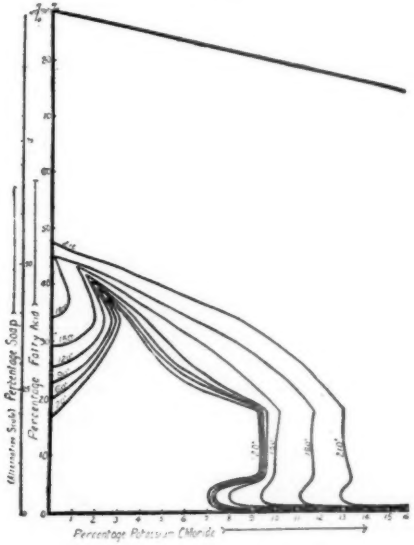
Solubility curves of potassium chloride and potassium oleate at 20°, 60°, 90°, 120°, 150°, 180°, *and* 210° *showing the extreme limits of the field of homogeneous isotropic solutions capable of existing at these temperatures. The point M is the only concentration at which middle soap can exist up to* 183°; *above this temperature it is isotropic.*

lye, is briefly discussed, and it is shown that it is confined to a negligibly narrow region. This is again the finding in the present case, but since a few instances have been met with where apparently these three phases stably co-exist over a very narrow range, corresponding provision has been made in Figs. 2 and 3 of the present paper by indicating the very narrow triangle connecting the compositions of these three phases immediately to the right of the projecting portion of the isotropic field. In Fig. 2 of the previous paper this triangle was represented by a single heavy tie-line, whereas, through inadvertence, in Fig. 1 it was omitted altogether.

For practical purposes, whether this region is a single line or such a very narrow triangle is of no importance.

M. C. Field attempted to test this question for us by preparing five solutions each of which was $0{\cdot}5N_w$-potassium oleate and contained amounts of total potassium chloride ranging from $1{\cdot}70N_w$ to $1{\cdot}99N_w$. All five exhibited three layers, the proportion of the middle layer being greatest in the first and progressively less in the others and the amount of upper layer changing accordingly. This would at first sight appear to establish the existence of the suggested

FIG. 5.



Limits of existence, in technical units, of homogeneous isotropic solutions containing potassium chloride and potassium oleate at 20°, 60°, 90°, 120°, 180°, *and* 210°, *showing the two regions in which solutions of pure soap form isotropic solutions at* 210°.

triangular field and give it a maximum width on the diagram extending from fractional proportion of potassium chloride = 0·53 to 0·57. However, the refractive index of the lye as well as of the middle layer changed progressively with the total composition of the system instead of each phase being identical in composition for all cases and varying only in amount. This is, then, direct proof that complete equilibrium was not attained and that the suggested triangle must be much narrower, having a width of only 1% or so of the total width of the diagram.

Figs. 4 and 5 present the isotherms which bound the field of

isotropic solutions at various temperatures from room temperature up to 210°. These have been much more carefully worked out than in the case of palmitate, and in addition to the actual experimental points indicated in the diagram the position of the isotherms was checked by a series of graphs representing cross sections of the triangular space model for various normalities of soap.

Whereas the maximum temperatures at which middle soap can exist are lowered by the addition of salt, sections 11 and 13 of Table II indicate that in neat soap they are not much affected.

Summary.

1. The equilibria between the various forms of a potassium soap are very similar to those for a sodium soap.

2. All the soap phases that exist in the three-component system, including salt, are found in the simpler system, soap and water, where also their separation is spontaneous; that is, they "salt out" in the absence of salt and may even be observed at room temperature.

3. The limits of the field of existence of isotropic liquid solutions of potassium oleate with and without potassium chloride have been accurately determined for temperatures up to 210°. This single phase includes wholly crystalloidal solutions and ranges at sufficiently high temperatures from pure water up to pure anhydrous liquid potassium oleate, the two being miscible in all proportions above 300°.

4. Improvements in the methods of optical investigation have enabled progress to be made with the delimitation of the two important anisotropic liquids, neat soap and middle soap. Both neat soap and middle soap are typical conic anisotropic liquids.

Our warm thanks are due to Messrs. Chris. Thomas and Bros., Ltd., who supported this work by awarding to one of us (W. J. E.) a Colston Research Fellowship.

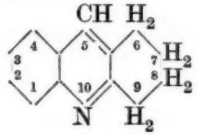
THE UNIVERSITY, BRISTOL. [*Received, November 12th,* 1925.]

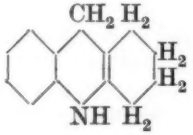
LVI.—*Tetrahydroacridine, Octahydroacridine, and their Derivatives. Part II. Resolution of the Octahydroacridines (A) and (B).*

By WILLIAM HENRY PERKIN, jun., and WILLIAM GREENWELL SEDGWICK.

IN Part I of this investigation (Perkin and Sedgwick, J., 1924, **125**, 2437) it was shown that the reduction of tetrahydroacridine (I) with tin and hydrochloric acid leads at once to the formation of

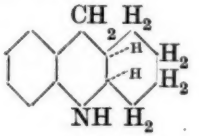
two octahydroacridines (A, m. p. 82°, and B, m. p. 72°), four atoms of hydrogen being absorbed. It is remarkable that, in spite of careful search, no intermediate product of reduction could be detected, because it was to be expected that the carbon-nitrogen conjugated system ·C:C·C:N· would, in the first place, absorb two atoms of hydrogen to yield a hexahydroacridine (II) containing the grouping, ⩾C·C:C·N·.

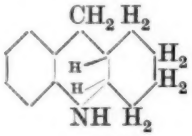
(I.) 

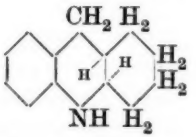
 (II.)

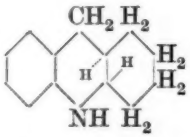
Experiment showed that, if less reducing agent is employed than is necessary to convert the whole of the tetrahydroacridine into octahydroacridine, the product is a mixture of octahydroacridine and unchanged tetrahydroacridine. If, as may be assumed to be the case, hexahydroacridine (II) is the intermediate stage, it is probable that this substance is more readily reduced than tetrahydroacridine and is therefore at once converted into octahydroacridine, the corresponding amount of tetrahydroacridine remaining unchanged. It was pointed out in the previous communication (p. 2440) that remarkable as the observation seemed at first, the formation of two octahydroacridines by the addition of four atoms of hydrogen to tetrahydroacridine (I) is strictly in accordance with structural theory.

If the model (compare Sachse, *Ber.*, 1890, **23**, 1363; Mohr, *J. pr. Chem.*, 1918, **98**, 315) be set up and examined, it is at once evident that the pairs (III) and (IV) should result from the addition

(III.) 



(IV.) 



of four hydrogen atoms to tetrahydroacridine and that both pairs should be resolvable into their *d*- and *l*-constituents. In order to prove that the configurations (III) and (IV) actually represent the two octahydroacridines (A) and (B), it was clearly necessary to demonstrate that both these substances can be resolved into active constituents. In our first experiments, resolution was attempted

with the aid of bromocamphorsulphonic acid, but without immediate success. It was then discovered that the salts of (A) and (B) with the *d*- and *l*-camphorsulphonic acids are sufficiently well characterised to allow of satisfactory fractional crystallisation, and in this way resolution was achieved in both cases. When the pure salts were decomposed by alkali, they at once yielded the *d*- and *l*-modifications of the *octahydroacridines* (*A*) and (*B*) in a pure state.

The stages in these resolutions will be clearly understood from the following tables:

(I) *Resolution of* dl-*Octahydroacridine* (*A*, m. p. 82°).

d-Camphorsulphonic acid	*l*-Camphorsulphonic acid
↓	↓
l-*Octahydroacridine* (*A*) d-*camphorsulphonate* (m. p. 183°)	d-*Octahydroacridine* (*A*) l-*camphorsulphonate* (m. p. 182°)
NaOH ↓	NaOH ↓
l-*Octahydroacridine* (*A*), m. p. 85°, $[\alpha]_D$ −32°.	d-*Octahydroacridine* (*A*), m. p. 84·5°, $[\alpha]_D$ +34°.

Mean rotation $[\alpha]_D$ ±33°.

(II) *Resolution of* dl-*Octahydroacridine* (*B*, m. p. 72°).

d-Camphorsulphonic acid	*l*-Camphorsulphonic acid
↓	↓
l-*Octahydroacridine* (*B*) d-*camphorsulphonate* (m. p. 172°)	d-*Octahydroacridine* (*B*) l-*camphorsulphonate* (m. p. 172°)
NaOH ↓	NaOH ↓
l-*Octahydroacridine* (*B*), m. p. 73°, $[\alpha]_D$ −24°.	d-*Octahydroacridine* (*B*), m. p. 73°, $[\alpha]_D$ +22°.

Mean rotation $[\alpha]_D$ ±23°.

When the corresponding *d*- and *l*-modifications are mixed, the inactive forms are at once produced, but loss of activity also occurs gradually when the *d*- or *l*-modifications are heated at or above their melting points and the change to the inactive form is complete on distillation under reduced pressure. It is curious, both in the case of (A) and of (B), that the inactive modification melts at a somewhat lower temperature than the active constituents, suggesting that the *dl*-modification may be a mixture and not a true racemic compound. It is interesting also that, on boiling with acetic anhydride, *l*-octahydroacridine (A) is converted into the acetyl derivative of *dl*-octahydroacridine (A) (m. p. 86°) described in the previous communication (p. 2449).

So far, sufficient evidence is not available to enable definite configurations to be assigned to the octahydroacridines (A) and (B),

but it is significant that, when tetrahydroacridone is reduced by sodium amalgam (*loc. cit.*, p. 2449), the product consists entirely of modification (A). The probability in this reduction is that the hydrogen atoms will add themselves on to the double linking in the direction indicated in (III) and we are for this reason inclined to assign the configuration (III) to octahydroacridine (A). In the earlier communication (p. 2450) it is shown that isatin condenses with *cyclo*hexanone to yield tetrahydroacridinecarboxylic acid (compare Borsche, *Ber.*, 1908, **41**, 2207) and that this acid yields, on reduction with sodium amalgam, a mixture of octahydroacridinecarboxylic acids (A) and (B), which, on distillation, decompose with elimination of carbon dioxide and formation of the octahydroacridines (A) and (B). These acids are doubtless also *dl*-modifications corresponding to (III) and (IV) and experiments on their resolution are in progress.

During the course of these resolution experiments, we thought it desirable to be able to confirm the results obtained with the octahydroacridines (A) and (B) by the investigation of another case of the same kind. We therefore condensed 1-methyl*cyclo*hexan-3-one with (i) *o*-aminobenzaldehyde and (ii) isatin. In (i) we obtained a substance melting at 71° which may be either 6- or 8-*methyltetrahydroacridine* and in (ii) a 6(or 8)-*methyltetrahydroacridinecarboxylic acid* (m. p. 296°) which, on heating, yielded the same parent substance melting at 71°. When this substance is reduced with tin and hydrochloric acid, it is converted into a mixture of 6(or 8)-*methyloctahydroacridines* (*A*, m. p. 92°) and (*B*, m. p. 80°), and again (compare above) only the modification (A) is produced when 6(or 8)-methyltetrahydroacridone (*loc. cit.*, p. 2442) is reduced with sodium amalgam. Of these modifications, the substance (A) has been resolved with the aid of the *d*- and *l*-camphorsulphonic acids and the active modifications have $[\alpha]_D + 20°$ and $- 28°$, respectively, or a mean rotation of $[\alpha] \pm 24°$.

EXPERIMENTAL.

The *l*-camphorsulphonic acid used in this research was prepared by sulphonating *l*-camphor with a mixture of sulphuric acid and acetic anhydride as described by Reychler (*Bull. Soc. chim.*, 1898, **111**, 120). The *d*-acid was supplied by the British Drug Houses. Both gave physical constants in good agreement with those quoted in the literature, melting, in the anhydrous form, at 193° and showing, in solution as ammonium salts, $[\alpha]_D \pm 19{\cdot}9°$. The octahydroacridine (A) (m. p. 82°) used in the following experiments was obtained partly by the reduction of tetrahydroacridone with sodium amalgam, and both the (A) and (B) modifications were prepared

in quantity by the reduction of tetrahydroacridine and separated by the sulphuric acid method (compare Perkin and Sedgwick, *loc. cit.*, p. 2448).

Resolution of dl-*Octahydroacridine* (*A*) (m. p. 82°).—This *dl*-base (20 g.), dissolved in the minimum quantity of hot alcohol, was added to a concentrated solution of the equivalent quantity of *d*-camphorsulphonic acid (24·9 g.), and the mixture left over-night. The mother-liquor was then decanted from the crystalline mass of crude l-*octahydroacridine* (*A*) d-*camphorsulphonate*, the crystals (24 g.) were quickly washed with a little alcohol, dissolved in the minimum quantity of boiling alcohol, and allowed to recrystallise. This operation was repeated four times, the final product, l-*octahydroacridine* (*A*) d-*camphorsulphonate* (8 g.), separating in large, colourless prisms, m. p. 182° (Found: C, 65·4; H, 7·7. $C_{13}H_{17}N,C_{10}H_{15}O{\cdot}SO_3H$ requires C, 65·9; H, 7·9%; 0·6084 required 14·55 c.c. of *N*/10-NaOH for neutralisation, whereas the theoretical amount is 14·5 c.c.).

In order to separate the free base, the salt was dissolved in alcohol, and the solution carefully neutralised with *N*/10-sodium hydroxide, phenolphthalein being used as indicator; the precipitation was then completed by the addition of water, and the base extracted three times with ether. The ethereal extract was dried over sodium sulphate and concentrated; l-*octahydroacridine* (*A*) then separated slowly in well-defined plates, m. p. 85° (Found: C, 83·2; H, 9·1. $C_{13}H_{17}N$ requires C, 83·4; H, 9·1%). 0·5 G. in 20 c.c. of alcohol ($c = 2{\cdot}5$) gave, in a 1-dcm. tube, $\alpha - 0{\cdot}80°$, whence $[\alpha]_D = -32°$.

d-*Octahydroacridine* (*A*) was isolated in the same manner by means of *l*-camphorsulphonic acid and melted at 84·5° (Found: C, 83·0; H, 9·0%). $[\alpha]_D$ in alcohol, + 34° ($c = 2{\cdot}5$) and in acetone, + 29° ($c = 2{\cdot}0$). Both active modifications undergo racemisation on distillation and when equal quantities were mixed and the mixture was crystallised from ether, the *dl*-base (A) obtained melted at 82·5°. The melting point of a mixture of approximately equal quantities was 83°. The mother-liquor from the first crystallisation of *l*-octahydroacridine (A) *d*-camphorsulphonate deposited, on further concentration, several crops of crystals of varying rotation. The last of these, on repeated recrystallisation, yielded ultimately a crop which was nearly pure d-*octahydroacridine* (*A*) d-*camphorsulphonate* (m. p. 180°), since the base, set free on neutralisation, had, in alcohol, $[\alpha]_D$ + 25°.

Resolution of dl-*Octahydroacridine* (*B*) (m. p. 72°).—This *dl*-base (10 g.) was slowly dissolved in a warm concentrated aqueous solution of *d*-camphorsulphonic acid (15 g.), the excess of acid over

that theoretically required to neutralise the base (12·4 g.) being necessary to effect complete solution. After 12 hours, the crystalline mass was collected, washed with alcohol, and dried between blotting paper, the filtrate (O) being preserved for subsequent treatment.

The crude l-*octahydroacridine* (*B*) d-*camphorsulphonate* crystallised from water with one molecule of the solvent, which was removed by drying in a desiccator over sulphuric acid or by heating in an air-oven.

The salt was then subjected to two crystallisations from alcohol; the ultimate yield of pure anhydrous *l*-octahydroacridine (B) *d*-camphorsulphonate was 4 g. and the salt melted at 172° with previous softening. 0·4693 G. of the salt required 11·1 c.c. of *N*/10-sodium hydroxide for neutralisation, whereas the theoretical amount is 11·2 c.c.

l-*Octahydroacridine* (*B*) was obtained from this salt by neutralisation with sodium hydroxide and separated from petroleum (b. p. 40—60°) in colourless plates, m. p. 73° (Found: C, 83·1; H, 9·5. $C_{13}H_{17}N$ requires C, 83·4; H, 9·1%). $[\alpha]_D$ in alcohol ($c = 2·5$), − 24°; $[\alpha]_D$ in acetone ($c = 1·0$), − 19°.

The filtrate (O), after removal of the crystals which had separated on further standing, was neutralised with sodium hydroxide, and the precipitated base extracted with ether. The ethereal extract was evaporated in a vacuum desiccator, and the crystalline residue (4 g.) showed a small dextrorotation in alcoholic solution.

This material was combined with *l*-camphorsulphonic acid under the conditions already described, the salt purified by repeated crystallisation, and the d-*octahydroacridine* (*B*) precipitated by neutralisation with sodium hydroxide. The base melted at 73° and had $[\alpha]_D$ in alcohol ($c = 2$) + 22°.

The salts of octahydroacridine (B) with the camphorsulphonic acids are more soluble than those of the isomeride (A), particularly in anhydrous alcohol. This property may be utilised as a method for the separation of the two isomerides, in which case the mixture resulting from the reduction of tetrahydroacridine with tin and hydrochloric acid (*loc. cit.*, p. 2448) is dissolved in a warm concentrated alcoholic solution of the equivalent quantity of *d*-camphorsulphonic acid and allowed to crystallise. The first crop of crystals consists of almost pure octahydroacridine (A) *d*-camphorsulphonate and can be used directly for the resolution of the base.

6(or 8)-*Methyltetrahydroacridine*.—In preparing this substance, a mixture of *o*-aminobenzaldehyde (3 g.) with 1-methyl*cyclo*hexan-3-one (5 g.) was heated in an oil-bath at 100° for about an hour and then at 130° for 1½ hours. On distilling the product under

reduced pressure (15 mm.), water and unchanged methyl*cyclo*hexanone passed over below 120° and then *methyltetrahydroacridine* (3 g.) distilled at about 150° as a pale yellow oil which quickly solidified. The base crystallised from petroleum in colourless plates, m. p. 70—71° (Found: C, 85·0; H, 7·5. $C_{14}H_{15}N$ requires C, 85·3; H, 7·6%). The *picrate*, prepared by mixing solutions of the base and picric acid in hot alcohol, crystallised on cooling in yellow prisms, m. p. 182° (darkening).

6(or 8)-*Methyltetrahydroacridinecarboxylic Acid.*—A solution of isatin (10 g.) in potassium hydroxide (42 c.c. of 30%) was mixed with alcohol (80 c.c.) and 1-methyl*cyclo*hexanone (20 g.) and refluxed for 12 hours. The alcohol was evaporated in an open basin, the viscid residue mixed with water, the semi-crystalline scum removed by filtration, and the *methyltetrahydroacridinecarboxylic acid* precipitated as a fine, yellow, crystalline powder by the addition of 50% acetic acid.

The dried product is pure enough for most purposes and is very sparingly soluble in the usual solvents. It separates from much alcohol in minute, yellow needles, m. p. 296° (decomp.) (Found: C, 74·8; H, 6·6. $C_{15}H_{15}O_2N$ requires C, 74·7; H, 6·2%). The acid (10 g.) was heated in a distilling flask at its melting point until evolution of carbon dioxide had ceased and the dark liquid was then distilled under 15 mm. pressure; 6(or 8)-*methyltetrahydroacridine* passed over as a pale yellow oil which immediately crystallised. The recrystallised material melted at 70—72° and gave no depression of melting point when mixed with a specimen prepared by the *o*-aminobenzaldehyde process just described.

The 6(or 8)-*Methyloctahydroacridines.*—Methyltetrahydroacridine was reduced with tin and hydrochloric acid under the conditions described in the case of tetrahydroacridine (*loc. cit.*, p. 2448), and the resulting two methyloctahydroacridines (A) and (B) were separated in a manner similar to that employed in the separation of the octahydroacridines (A) and (B) (*loc. cit.*). *Methyloctahydroacridine* (*A*) was also obtained by the reduction of methyltetrahydroacridone and separated from ether or petroleum in colourless prisms, m. p. 92°. It was resolved with the aid of *d*- and *l*-camphorsulphonic acids exactly as described in the case of the octahydroacridines (A) and (B). The *d*- and *l*-isomerides melt at 92° (Found for the *d*-isomeride: C, 83·4; H, 9·4. $C_{14}H_{19}N$ requires C, 83·6; H, 9·5%). 0·09 G. of the *d*-modification, dissolved in 15 c.c. of alcohol ($c = 0·6$), gave in a 1-dcm. tube, $\alpha = +0·12°$, whence $[\alpha]_D + 20°$. 0·1 G. of the *l*-modification, dissolved in 20 c.c. of alcohol ($c = 0·5$), gave in a 2-dcm. tube, $\alpha - 0·28°$, whence $[\alpha]_D - 28°$; the mean rotation is therefore $[\alpha]_D \pm 24°$.

The *sulphate* of *dl*-methyloctahydroacridine (B) is more readily soluble than the sulphate of the modification (A), and the base melts at 80°; no attempt was made to resolve it into its active modifications.

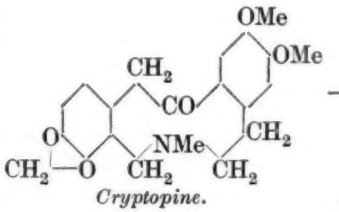
One of us (W. G. S.) desires to express his thanks to the Salters' Institute of Industrial Chemistry for a Fellowship which has enabled him to engage in this investigation.

THE DYSON PERRINS LABORATORY, OXFORD.
UNIVERSITY COLLEGE, LONDON. [*Received, December 28th*, 1925.]

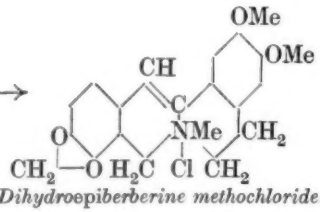
LVII.—*The Conversion of Berberine into β-Homochelidonine* (α-allo*Cryptopine*).

By ROBERT DOWNS HAWORTH and WILLIAM HENRY PERKIN, jun.

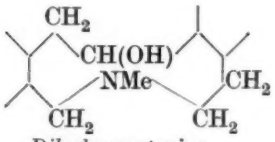
DURING the course of the investigation of cryptopine and protopine (Perkin, J., 1916, **109**, 815; 1918, **113**, 493, 722; 1919, **115**, 713) it was shown that these alkaloids contain a ten-membered ring, and that cryptopine and dihydrocryptopine are converted into quaternary chlorides, containing the berberine skeleton, when they are treated with phosphorus oxychloride:



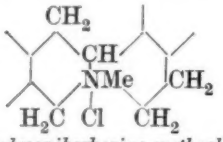
Cryptopine.



Dihydroepiberberine methochloride.



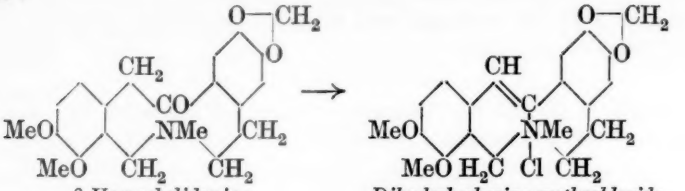
Dihydrocryptopine.



Tetrahydroepiberberine methochloride.

Subsequently Gadamer (*Arch. Pharm.*, 1919, **257**, 298; 1920, **258**, 148) found that β-homochelidonine, one of the alkaloids occurring in *Sanguinaria canadensis* and *Chelidonium majus*, is converted into dihydroberberine methochloride, and dihydro-β-homochelidonine into tetrahydroberberine methochloride under similar conditions. Gadamer therefore concluded that β-homochelidonine must, like cryptopine, contain a ten-membered ring and that the

change into dihydroberberine methochloride is to be represented thus:

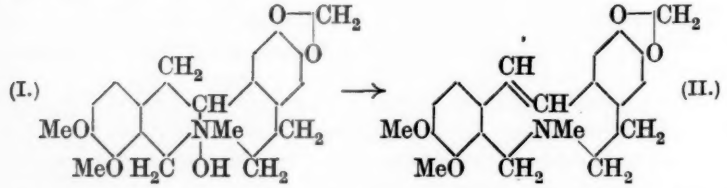


β-Homochelidonine. *Dihydroberberine methochloride.*

It is in view of this close relationship that Gadamer (*loc. cit.*) suggested the name *α-allo*cryptopine for β-homochelidonine.

The synthesis of berberine recently achieved by Perkin, Ray, and Robinson (J., 1925, **127**, 740; compare Späth, *Ber.*, 1925, **58**, 2268) will, it is hoped, serve as a basis for the synthesis of other alkaloids of similar constitution and it now became important to devise a method which would enable synthetical alkaloids of the berberine type to be converted into alkaloids like cryptopine, protopine, and β-homochelidonine with which they are clearly closely allied. The present investigation is concerned with such a method, namely, with the conversion of berberine into β-homochelidonine. The development of the process to the synthesis of cryptopine and the allied alkaloids will, it is hoped, form the subject of future communications.

It has long been known (Voss and Gadamer, *Arch. Pharm.*, 1910, **248**, 43; Freund, *Annalen*, 1913, **397**, 1; Pyman, J., 1913, **103**, 817; McDavid, Perkin, and Robinson, J., 1912, **101**, 1220; Perkin, J., 1916, **109**, 952) that tetrahydroberberine methohydroxide (I) loses water when its aqueous solution is evaporated in a vacuum and yields as chief product anhydrotetrahydromethylberberine (anhydromethylcanadine) (II), a remarkable change which results in the formation of a substance containing a ten-membered ring and in which the various groups occupy the same relative positions as in β-homochelidonine.

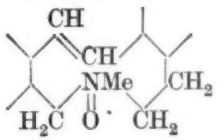


It is clearly only necessary to convert the group ·CH:CH· in the latter formula into ·CO·CH$_2$· in order to achieve the synthesis of β-homochelidonine.

The realisation of this comparatively simple change proved to be a very difficult problem, mainly because the usual methods are not applicable to anhydrotetrahydromethylberberine. This substance exhibits a remarkable tendency, when treated with many of the usual reagents, and indeed merely on boiling with alcohol or chloroform, to revert to tetrahydroberberine methohydroxide or its salts with consequent loss of the ten-membered ring (compare Pyman, *loc. cit.*, p. 834). We observed the same change when an ice-cold solution of the base in chloroform was treated with bromine, since the crystalline perbromide which separated yielded tetrahydroberberine methobromide on decomposition with sulphurous acid. A series of experiments on the action of oxidising agents on anhydrotetrahydromethylberberine did not lead to the desired result, although interesting oxidation products were obtained, when this base was treated with silver hydroxide or hydrogen peroxide, which will be discussed in a future communication.

Some years since (*Ber.*, 1909, **42**, 4811; 1910, **43**, 959), Prileshajew carried out an important piece of work in the course of which he showed that ethylene derivatives, ·CH=CH·, yield ethylene oxides, ·CH(O)CH·, on treatment with perbenzoic acid, and it seemed probable that, if this change could be brought about in the case of anhydrotetrahydromethylberberine, the resulting ethylene oxide grouping might be made to isomerise to ·CO·CH_2· and thus lead to the formation of β-homochelidonine (compare Weitz and Scheffer, *Ber.*, 1921, **54**, 2344).

When an ice-cold solution of the base (II) in chloroform is added to an ice-cold solution of perbenzoic acid, the ethylene oxide derivative does not appear to be produced. Oxidation takes place rapidly, however, and a base, $C_{21}H_{23}O_5N$, isomeric but not identical with β-homochelidonine, is obtained in good yield. This curious substance crystallises from water, decomposes at 135°, and yields a hydrochloride, $C_{21}H_{23}O_5N,HCl$, which is sparingly soluble in water. These and other properties seem to indicate that it is an amine oxide containing the group



(III.)

In connexion with the formation and properties of this substance, it is interesting to note that Meisenheimer (*Ber.*, 1919, **52**, 1667) has observed that perbenzoic acid converts methylallylaniline into the amine oxide, CH_2:CH·CH_2·NMePh:O, without affecting the

ethylenic linking of the allyl group. He shows that this amine oxide undergoes a curious isomeric change to phenylmethylallylhydroxylamine, $CH_2{:}CH{\cdot}CH_2{\cdot}O{\cdot}NMePh$, when heated with alkalis, and Bamberger and Leyden (*Ber.*, 1901, **34**, 12) state that dimethylaniline oxide is converted into a mixture of *o*- and *p*-dimethylaminophenol by contact with sulphuric acid.

These curious isomeric changes encouraged us to examine in detail the action of various reagents on anhydrotetrahydromethylberberine oxide (III) and it was ultimately observed that in the presence of glacial acetic acid and hydrochloric acid, this amine oxide isomerises to a basic substance which crystallises from ethyl acetate in colourless prisms, m. p. 160—161°, and is identical with β-homochelidonine. The synthetic alkaloid gave no depression in m. p. when mixed with a specimen of β-homochelidonine, for which we are indebted to Professor Gadamer; the hydrochloride was readily soluble in water and crystallised from alcohol–ether in colourless needles which were identical in appearance and behaviour with the hydrochloride of the naturally occurring alkaloid. The garnet-red aurichloride, m. p. 190—192° (decomp.), had all the properties of the double salt prepared from the natural product, whilst the colour reactions of the synthetic and the natural alkaloid with concentrated sulphuric acid, Fröhde's, and Erdmann's reagents were indistinguishable. We propose to investigate the mechanism of the above synthesis, more particularly in regard to the action of other reagents on the amine oxide, and details of this work as well as of the extension of the method to the synthesis of cryptopine, protopine, and allied alkaloids are reserved for a later communication.

Experimental.

Anhydrotetrahydromethylberberine was prepared as recommended by Pyman (*loc. cit.*, p. 833), but we found it advisable to use as little excess of silver hydroxide as possible in the preparation of tetrahydroberberine methohydroxide. Tetrahydroberberine methiodide, dissolved in boiling water, is agitated for ½ hour with the calculated amount of silver hydroxide, and the solution is filtered hot and tested for unchanged methiodide with silver nitrate. If iodide is still present, a further small quantity of silver hydroxide is added and the process repeated if necessary. The whole is then filtered and the solution evaporated exactly as described by Pyman. The perbenzoic acid used in these experiments was prepared by the method of Baeyer and Villiger (*Ber.*, 1900, **33**, 1575). It was extracted with ether and the content of the ethereal solution

estimated, immediately before use, by titration with potassium iodide and *N*/10-sodium thiosulphate.

Anhydrotetrahydromethylberberine Oxide. — Anhydrotetrahydromethylberberine (2 g.), dissolved in dry chloroform, was gradually added to a solution of perbenzoic acid (estimated as 1·8 g.) in ether (100 c.c.), maintained below 5° by immersion in ice. An oil gradually separated which sometimes crystallised on standing. After remaining over-night, the mixture was shaken with 10% sodium hydroxide; the amine oxide then solidified as a white solid (1·5 g.) and was collected after several hours. A second crop may be obtained from the filtrate by the careful addition of strong sodium hydroxide.

Anhydrotetrahydromethylberberine oxide crystallises from water in colourless, slender prisms, m. p. 135° (decomp.) (Found: C, 68·1; H, 6·5. $C_{21}H_{23}O_5N$ requires C, 68·3; H, 6·2%). It is soluble in chloroform or acetic acid, moderately easily soluble in ethyl acetate, and almost insoluble in ether or petroleum. It dissolves in hot water, but is less soluble in sodium hydroxide solution. On cooling the solution of the base in hot dilute hydrochloric acid, the *hydrochloride* separates in colourless nodules, m. p. 203° (decomp.) with previous darkening. It is more soluble in water than in dilute hydrochloric acid (Found: C, 62·2; H, 6·0. $C_{21}H_{23}O_5N,HCl$ requires C, 62·1; H, 5·9%).

β-*Homochelidonine.*—The amine oxide (1·5 g.), dissolved in glacial acetic acid (10 c.c.) and concentrated hydrochloric acid (5 c.c.), was heated in rapidly boiling water for an hour, the pale yellow solution diluted with water, made alkaline with potassium hydroxide,* and the cream-coloured solid collected. This was dissolved in methyl alcohol (20 c.c.), mixed with ether (200 c.c.), the ethereal solution washed with water until free from methyl alcohol, rapidly dried over potassium carbonate, and concentrated to a small bulk. On standing, β-homochelidonine separated; it crystallised from ethyl acetate in brilliant, colourless, monoclinic prisms, m. p. 160—161° (Found: C, 68·3; H, 6·5. Calc. for $C_{21}H_{23}O_5N$: C, 68·3; H, 6·2%). The crystals were exactly like those of a specimen of β-homochelidonine which Professor Gadamer very kindly sent us and there was no change in melting point when the two specimens were mixed.

Synthetic β-homochelidonine dissolves in concentrated sulphuric

* The base is not completely precipitated from its salts by the addition of ammonia, and this property of β-homochelidonine is made use of in the isolation of the alkaloid from the plant (Schmidt and Selle, *Arch. Pharm.*, 1890, **228**, 441).

acid to a yellow solution which rapidly becomes violet and slowly changes to bright red. With Fröhde's reagent, a yellow solution is obtained which soon becomes violet and then passes through brilliant blue to bluish-green. The base dissolves in Erdmann's reagent to a yellow solution which rapidly becomes violet and then dirty violet. These colour reactions are indistinguishable from those exhibited by the specimen of naturally occurring β-homochelidonine under similar conditions. The hydrochloride was obtained by dissolving the base in dilute hydrochloric acid and evaporating to dryness. The residue dissolved readily in alcohol and, on addition of ether, the hydrochloride slowly separated in slender, colourless, silky needles which turn yellow and shrink at about 170° and decompose at about 190°. The hydrochloride of the natural alkaloid possessed identical properties. The aurichloride separated on addition of gold chloride to the solution of the base in dilute hydrochloric acid, and crystallised from alcohol in warts of garnet-red crystals, m. p. 190—192° (decomp.). No alteration in m. p. was observed when this sample was mixed with the garnet-red aurichloride prepared in the same way from natural β-homochelidonine.

One of us (R. D. H.) desires to thank the Commissioners of the 1851 Exhibition for a studentship, and the Government Grant Committee of the Royal Society and the Research Fund Committee of the Chemical Society for grants towards the expense of this investigation.

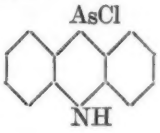
THE DYSON PERRINS LABORATORY,
OXFORD. [*Received, December 28th*, 1925.]

LVIII.—10-*Chloro*-5:10-*dihydrophenarsazine and its Derivatives. Part I. The Synthesis, Preparation, and Some Properties of* 10-*Chloro*-5:10-*dihydrophenarsazine.*

By HAROLD BURTON and CHARLES STANLEY GIBSON.

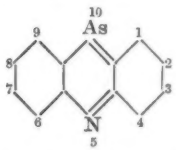
THE reaction between arsenious halides and secondary aromatic amines was the subject of a patent of F. Bayer & Co. (D.R.-P. 281049, Friedländer, "Fortschritte," 1914, XII, 843), and Wieland and Rheinheimer (*Annalen*, 1921, **423**, 1) made a comprehensive study of the derivatives of the compound obtained by condensing arsenious chloride and diphenylamine. To this compound, Wie-

land and Rheinheimer gave the name " phenarsazine chloride " and ascribed to it the constitution



which is the same as that ascribed to it by the patentees.*

* Wieland and Rheinheimer (*loc. cit.*) prepared the compound phenarsazine, which undoubtedly has the structure



The product of the reaction between diphenylamine and arsenious chloride is derived from phenarsazine by the addition of hydrogen chloride. This compound has hitherto been variously known as " diphenylamine arsenious chloride " (Contardi, *Giorn. Chim. Ind. Appl.*, 1920, i, 11; ii, 100), " phenarsazine chloride " (Wieland and Rheinheimer, *loc. cit.*), and " 6-chlorophenarsazine " (Lee Lewis and Hamilton, *J. Amer. Chem. Soc.*, 1921, **43**, 2218; Lee Lewis, Lowry, and Bergeim, *ibid.*, p. 891). In systematically describing this class of compounds, the name phenarsazine is retained for the parent substance and the atoms are numbered as indicated. The product of the reaction between diphenylamine and arsenious chloride and its simple derivatives are regarded as substitution products of 5 : 10-dihydrophenarsazine, at present unknown. " Phenarsazinic acid," which is already in use for the oxidation product of these derivatives, still applies.

Although the patent referred to was taken out in 1913 and issued in the German Empire in December, 1914, the specification was not available in this country until September, 1920. Our knowledge of this type of heterocyclic compound up to 1918 was limited to that contained in a brief abstract of the patent, which referred only to the general reaction between arsenious chloride and diarylamines without mentioning any specific compound (*J. Soc. Chem. Ind.*, 1915, **34**, 636). It ought to be pointed out that Dr. W. C. Ball independently prepared the compound early in 1918 (unpublished report of the Anti-gas Department) by the action of arsenious chloride on diphenylamine and examined a number of its simpler derivatives. Professor G. T. Morgan in 1918 (unpublished report) also studied the reaction and prepared certain analogues of 10-chloro-5 : 10-dihydrophenarsazine. In preparing his " diphenylamine arsenious chloride," Contardi (*loc. cit.*) heated diphenylamine hydrochloride and arsenious oxide together in the proportions for the following reaction to take place :

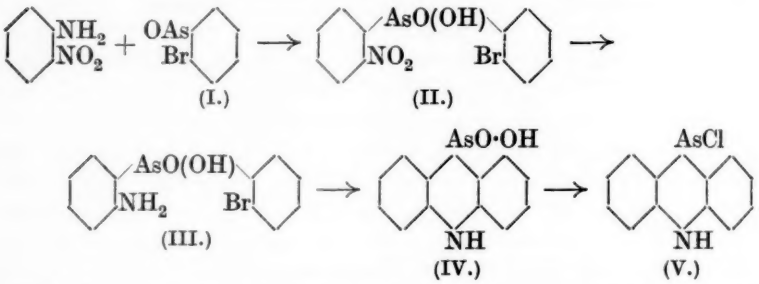
$$2NH(C_6H_5)_2,HCl + As_2O_3 = 2NH(C_6H_4)_2AsCl + 3H_2O.$$

The reaction as described by Contardi does take place, but we have not been able to obtain the high yield recorded, probably because the product of the reaction is decomposed rapidly by water at the temperature employed.

The compound so easily obtained in almost quantitative yield by heating

The work now described was in progress before the paper by Wieland and Rheinheimer (*loc. cit.*) was available, and it seems desirable to describe our results, which supplement those of these two workers.

The constitution ascribed to 10-chloro-5 : 10-dihydrophenarsazine has been proved to be correct by the following synthesis, which may be represented diagrammatically :



The first stage consisted in diazotising *o*-nitroaniline and coupling the diazo-compound with *o-bromophenylarsenious oxide* (I). The resulting compound, *2-bromo-6′-nitrodiphenylarsinic acid*, is reduced to the corresponding *amino*-compound (III) by means of ferrous hydroxide. By heating in amyl alcohol with potassium carbonate and a small quantity of copper powder, the amino-compound is readily converted into phenarsazinic acid (IV), and this, when reduced in hydrochloric acid–alcohol solution by sulphur dioxide, is readily converted into 10-chloro-5 : 10-dihydrophenarsazine identical with the substance prepared by the action of arsenious chloride on diphenylamine according to the equation

$$NH(C_6H_5)_2 + AsCl_3 = NH\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\rangle AsCl + 2HCl.$$

The preparation by Burton and Gibson (J., 1924, **125**, 2277) of the *N*-acetyl, *N*-propionyl, and *N*-benzoyl derivatives is confirmatory evidence of the presence of the :NH group in 10-chloro-5 : 10-dihydrophenarsazine.* Wieland and Rheinheimer (*loc. cit.*) also have described the preparation of the *N*-methyl derivative from

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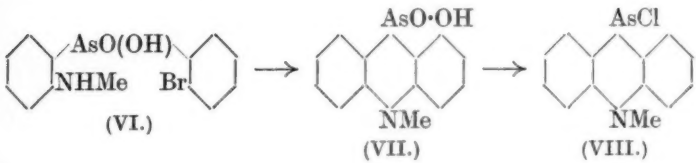
together arsenious chloride and diphenylamine under the conditions described by previous workers is systematically described as 10-chloro-5 : 10-dihydrophenarsazine.

* Whilst 10 : 10′-oxy-5 : 10-dihydrophenarsazine reacts with acetyl chloride to give 10-chloro-5-acetyl-5 : 10-dihydrophenarsazine, benzoyl chloride and the oxy-compound react quantitatively as follows :

$$[NH(C_6H_4)_2As]_2O + 2C_6H_5{\cdot}COCl = 2NH(C_6H_4)_2AsCl + (C_6H_5{\cdot}CO)_2O.$$

arsenious chloride and *N*-methyldiphenylamine. In connexion with our work on the phenarsazinic acids of this group of compounds, it was important to prepare the corresponding acid (Burton and Gibson, *loc. cit.*) with a view to investigate its trypanocidal properties. The only substance we have obtained by condensing arsenious chloride with *N*-methyldiphenylamine and working up the product under the conditions described by Wieland and Rheinheimer is 10-chloro-5 : 10-dihydrophenarsazine and not 10-chloro-5-methyl-5 : 10-dihydrophenarsazine (the *N*-methyl derivative). The melting point of the material we isolated from this reaction (about 10% of the theoretical quantity) was unaffected on admixture with an authentic specimen of 10-chloro-5 : 10-dihydrophenarsazine. Whilst the melting point, quoted by Wieland and Rheinheimer, of the supposed *N*-methyl derivative is 203° (some 8—10° higher than that of 10-chloro-5 : 10-dihydrophenarsazine), its further characterisation is somewhat inconclusive.* Like Wieland and Rheinheimer, we have failed to obtain the *N*-methyl derivative by attempting to methylate 10-chloro-5 : 10-dihydrophenarsazine and we therefore attempted to synthesise the compound according to the following scheme based on the method for obtaining the parent substance :



(VI.) (VII.) (VIII.)

Whether the compound (VII) is actually formed we are unable to say, but when the product obtained by heating *2-bromo-6′-methylaminodiphenylarsinic acid* (VI) in amyl alcohol with potassium carbonate and copper powder is reduced in hydrochloric acid–alcohol solution with sulphur dioxide 10-chloro-5-10-dihydrophenarsazine, *o*-bromophenylarsenious chloride and methylaniline are obtained (see p. 459). While the *N*-acyl derivatives of 10-chloro-5 : 10-dihydrophenarsazine are prepared quite readily, the fact that we have been unable to prepare the *N*-methyl derivative either directly or by synthesis is not easily explained.

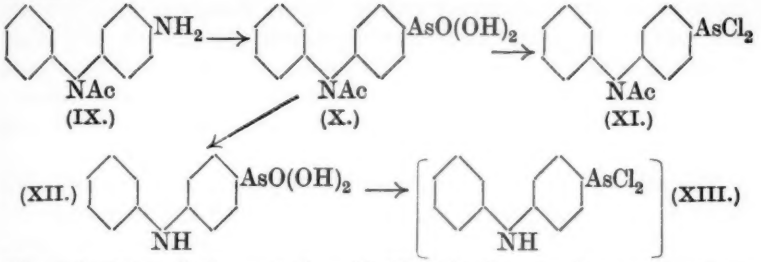
The most convenient way for preparing 10-chloro-5 : 10-dihydrophenarsazine in the laboratory is by heating one molecular proportion of diphenylamine with rather more than one molecular proportion of freshly distilled arsenious chloride in dichlorobenzene. The

* The micro-analysis quoted by the above authors showed a nitrogen content of 5·0%, the calculated values for $NH(C_6H_4)_2AsCl$ and $NMe(C_6H_4)_2AsCl$ being 5·05 and 4·95% of nitrogen, respectively.

product crystallises from the solution on cooling and is rapidly purified by extraction with carbon tetrachloride. The fact that the reaction between arsenious chloride and diphenylamine takes place slowly at the ordinary temperature * (actually a yield of 10% of the theoretical was obtained after 16 months) has enabled us to study the reaction somewhat closely. When the two reacting substances are mixed in the presence of a solvent, a white, crystalline substance having the composition $HCl,NH(C_6H_5)_2,AsCl_3$, is slowly deposited. In a sealed apparatus no development of pressure was recorded, but the solution became dark green and crystals of 10-chloro-5 : 10-dihydrophenarsazine were slowly deposited. The same white crystalline substance was formed immediately on mixing diphenylamine hydrochloride and arsenious chloride, but no further reaction took place. On heating a mixture of arsenious chloride and diphenylamine or its hydrochloride in high-boiling solvents, the additive compound dissolves, a copious evolution of hydrogen chloride takes place, and 10-chloro-5 : 10-dihydrophenarsazine is rapidly formed. From these results, it appears that at the ordinary temperature diphenylamine and arsenious chloride react to liberate hydrogen chloride which combines with unchanged diphenylamine, forming its hydrochloride which then crystallises as the additive compound with arsenious chloride. The substitution product is soluble and has not been isolated, but it is clear that this soluble compound is intermediate in the formation of the final product. If the mixture is not heated and no escape for the hydrogen chloride is provided, it is obvious that the reaction cannot go to completion. In view of the results of the large number of investigations on the action of arsenious chloride on aniline (summarised by Schmidt, *J. Amer. Chem. Soc.*, 1921, **43**, 2449) it is quite probable that the soluble intermediate compound may have the composition $(C_6H_5)_2N{\cdot}AsCl_2$. The ease of formation of 10-chloro-5 : 10-dihydrophenarsazine is very striking in view of the fact that usually para-substitution takes place when arsenic is introduced into the nucleus of aromatic amines. This is the case, not only in the formation of arsanilic acid, but also when arsenious chloride reacts with dialkylanilines (Michaelis and Rabinerson, *Annalen*, 1892, **270**, 139; Michaelis, *Ber.*, 1908, **41**, 1514); with monoalkylanilines and arylglycines (Poulenc Frères and Oechslin, French Patents 450214, 462276, and 473704). The following scheme of reactions was therefore studied with a view to the preparation of *p*-phenylaminophenylarsenious chloride (diphenylamine-*p*-arsenious chloride), which obviously

* The investigation of the reaction between diphenylamine and arsenious chloride at the ordinary temperature was carried out by the late Mr. D. C. Vining and one of us (C. S. G.).

cannot be prepared directly from arsenious chloride and diphenylamine :

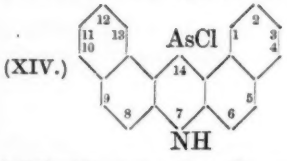


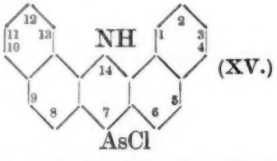
The reduction of the arsinic acid (XII) in the usual manner causes the elimination of the arsenic, and diphenylamine is the main product of the reaction. Consequently it has not been possible to prepare *p*-phenylaminophenylarsenious chloride (XIII), although its *N*-acetyl derivative (XI) is easily obtainable. In view of the ease with which 10-chloro-5 : 10-dihydrophenarsazine is obtained, this result is not unexpected.

In studying the action of arsenious chloride on aniline, Schmidt (*loc. cit.*) isolated trianilinoarsine hydrochloride, $(C_6H_5{\cdot}NH,HCl)_3As$, which was first described by Schiff (*Compt. rend.*, 1863, **56**, 268, 1095). By heating this compound for a long time, either alone or in the presence of an excess of aniline, Schmidt claimed to have obtained 10-chloro-5 : 10-dihydrophenarsazine, which he identified as the corresponding oxy-compound.* Schmidt states that the reaction which takes place may be expressed as follows :

$$(C_6H_5{\cdot}NH,HCl)_3As = NH(C_6H_4)_2AsCl + C_6H_5{\cdot}NH_2,HCl + NH_4Cl.$$

Since we have been able to isolate diphenylamine from the product obtained by heating the trianilinoarsine hydrochloride with an excess of aniline, it is possible that the formation of 10-chloro-5 : 10-dihydrophenarsazine may be due to the action of arsenious chloride on diphenylamine which is formed under these conditions. This possibility is supported by the fact that when arsenious chloride and β-naphthylamine are heated together in *o*-dichlorobenzene solution 14-*chloro*-14 : 7-*dihydrodibenzophenarsazine* (XIV)





* Schmidt states that the oxy-compound is crystallised from acetic acid. It has been known for some time (Wieland and Rheinheimer, *loc. cit.*) that under such conditions the oxy-compound is converted into the 10-acetyl-5 : 10-dihydrophenarsazine.

is readily obtained with elimination of ammonium chloride, and is identical with the product obtained by heating di-β-naphthylamine with arsenious chloride under identical conditions (D.R.-P., *loc. cit.*). α-Naphthylamine and arsenious chloride do not react to give a compound analogous to 10-chloro-5 : 10-dihydrophenarsazine; the compound *7-chloro*-7 : 14-*dihydrodibenzophenarsazine* (XV) is, however, readily obtained from di-α-naphthylamine (D.R.-P., *loc. cit.*).

The ease of the *oo'*-substitution in diphenylamine is also well illustrated by the preparation in good yield of 10 : 10'-oxy-5 : 10-dihydrophenarsazine from diphenylamine and arsenious oxide according to the equation:

$$2NH(C_6H_5)_2 + As_2O_3 = [NH(C_6H_4)_2As]_2O + 2H_2O.$$

The reaction takes place readily at temperatures above 130° in the presence of phosphorus pentoxide.

Regarding 10-chloro-5 : 10-dihydrophenarsazine, one of its most striking properties is its power of forming molecular compounds. Molecular compounds with acetic acid, *s*-tetrachloroethane, chlorobenzene, *o*-dichlorobenzene, acetone, carbon tetrachloride, and arsenious chloride have been isolated.

The chlorine atom in 10-chloro-5 : 10-dihydrophenarsazine can be easily replaced by other atoms or groups. Some of these derivatives have been described by Wieland and Rheinheimer (*loc. cit.*). The most convenient way of preparing the corresponding bromo- and iodo-compounds—we have not succeeded in preparing the latter compound directly from diphenylamine and arsenious iodide—is by adding the corresponding concentrated halogen acid to the solution of the oxy-compound in acetic acid. The bromo- and iodo-compounds are formed almost quantitatively in a state of purity. The iodo-compound resembles the chloro-compound in showing a similar tendency to form molecular compounds with, for example, benzene and acetic acid. Wieland and Rheinheimer noticed the solubility of the oxy-compound in methyl alcohol and isolated the colourless 10-methoxy-5 : 10-dihydrophenarsazine. The analogous n-*butoxy*- and *benzyloxy*-compounds described in the present paper are also colourless and being more soluble than the methoxy-derivative are more useful in preparing other derivatives, for example, the sulpho-compound.

EXPERIMENTAL.

o-*Bromophenylarsinic Acid*, $C_6H_4Br{\cdot}AsO(OH)_2$.—*o*-Aminophenylarsinic acid (36 g.) dissolved in hydrobromic acid (126 c.c.; *d* 1·265) and water (63 c.c.) was diazotised at 0° with sodium nitrite (12·6 g.)

in water (25 c.c.). The cold diazo-solution was added gradually, with stirring, to a solution of cuprous bromide at 30—40°. (The cuprous bromide solution was made by boiling 16·5 g. of copper carbonate, 165 c.c. of hydrobromic acid, and copper until the solution was clear.) The solid matter was filtered off, and extracted with hot alcohol. The alcoholic extract was evaporated to dryness, boiled with sodium carbonate solution and filtered. On acidifying with concentrated hydrochloric acid, *o*-bromophenylarsinic acid (27 g.) separated in nearly colourless crystals, m. p. 201° (decomp.). The acid crystallises from aqueous alcohol in colourless prisms, m. p. unchanged (Found: As, 26·4. Calc., As, 26·7%).

o-Bromophenylarsenious Oxide (I).—*o*-Bromophenylarsinic acid (14 g.) was dissolved in alcohol (14 c.c.) and concentrated hydrochloric acid (14 c.c.) containing a trace of iodine. Sulphur dioxide was passed into the boiling mixture for 30 minutes; the chloroarsine then separated as a heavy oil. After evaporation of the alcohol, the oil was extracted with benzene. The benzene solution was shaken with ammonia (14 c.c.; *d* 0·880) and, after the mixture had cooled, the solid matter was filtered off. This was washed with water until free from ammonium chloride and dried. The benzene filtrate on evaporation gave a small quantity of the oxide. The yield was 92·5% of the theoretical. *o-Bromophenylarsenious oxide* is insoluble in most neutral solvents and melts at 234—238° (Found: As, 30·25. C_6H_4OBrAs requires As, 30·4%).

2-Bromo-6′-nitrodiphenylarsinic Acid (II).—A suspension of *o*-nitroaniline (13·8 g.) in concentrated hydrochloric acid (80 c.c.) and water (250 c.c.) was cooled to 0° and diazotised with a solution of sodium nitrite (7·6 g.) in water. The filtered solution was added with stirring to a solution, at 20°, of *o*-bromophenylarsenious oxide (27·2 g.) in 5*N*-sodium hydroxide solution (174 c.c.) diluted to 500 c.c. with water, and containing 10 c.c. of 10% aqueous copper sulphate solution to which ammonia had been added to form the soluble complex. The mixture was stirred for 2 hours, made faintly acid to litmus, and filtered. On adding concentrated hydrochloric acid to the filtrate, until Congo-paper turned blue, *2-bromo-6′-nitrodiphenylarsinic acid* (19·6 g.) was precipitated. It crystallised from dilute alcohol in pale yellow prisms, m. p. 254—255° (decomp.) (Found: Br, 20·9; As, 19·2. $C_{12}H_9O_4NBrAs$ requires As, 19·4; Br, 20·7%).

2-Bromo-6′-aminodiphenylarsinic Acid (III).—Ferrous hydroxide was precipitated from a hot solution of ferrous sulphate (50 g.) in water (150 c.c.) by adding an excess of 25% sodium hydroxide solution. To the boiling suspension a solution of 2-bromo-6′-nitrodiphenylarsinic acid (11·5 g.) in dilute sodium hydroxide was added

slowly with stirring. The mixture was then boiled for 15 minutes. After filtration from the ferric hydroxide, the colourless solution was acidified with concentrated hydrochloric acid (Congo-paper), and the precipitated amino-acid (9·8 g.) filtered. It crystallised from dilute alcohol in colourless prisms, m.p. 213—214° (decomp.) (Found: As, 20·7; Br, 22·3. $C_{12}H_{11}O_2NBrAs$ requires As, 21·1; Br, 22·45%).

2-Bromo-6′-methylaminodiphenylarsinic Acid (VI).—2-Bromo-6′-aminodiphenylarsinic acid (21·4 g.) was suspended in water (150 c.c.) and mixed with 7·6 g. of methyl sulphate. After thorough mixing, a solution of sodium hydroxide (5 g.) in water (20 c.c.) was added in five portions at intervals of 30 minutes. The mixture was well shaken after each addition. The solution was then acidified with hydrochloric acid, and the crude acid filtered. This was dissolved in the minimum quantity of hot alcohol and allowed to cool; a crop of unchanged material (6·0 g.) was then obtained. The alcoholic solution was evaporated and a fraction (10·8 g.), m. p. 192—193°, obtained. This fraction on recrystallisation from alcohol melted at 193—194° (decomp.) (Found: C, 42·3; H, 3·7; Br, 21·6. $C_{13}H_{13}O_2NBrAs$ requires C, 42·2; H, 3·5; Br, 21·6%).

2-Bromo-6′-dimethylaminodiphenylarsinic Acid.—A mixture of 2-bromo-6′-aminodiphenylarsinic acid (4·3 g.) and methyl sulphate (10 c.c.) was heated on the steam-bath for 3 hours. After decomposition of the resulting solution with sodium carbonate solution, the acid was precipitated by hydrochloric acid. It crystallised from aqueous alcohol in clusters of colourless needles, m. p. 220—221° (decomp.) (Found: C, 43·8; H, 4·2; Br, 21·0. $C_{14}H_{15}O_2NBrAs$ requires C, 43·75; H, 3·9; Br, 20·8%).

The Formation of Phenarsazinic Acid (IV) *from 2-Bromo-6′-aminodiphenylarsinic Acid. Isolation of 10-Chloro-5:10-dihydrophenarsazine* (V).—A mixture of 2-bromo-6′-aminodiphenylarsinic acid (10·8 g.), dry potassium carbonate (4·4 g.), amyl alcohol (80 c.c.), and a trace of copper powder was boiled under reflux for 12 hours. The amyl alcohol was removed with steam, and the aqueous residue filtered from the copper. The solution was acidified with hydrochloric acid, and the precipitated acid (8·9 g.) filtered off, well washed with water, and dissolved in a mixture of alcohol (20 c.c.) and concentrated hydrochloric acid (20 c.c.) containing a trace of iodine. Sulphur dioxide was passed into the boiling solution for 10 minutes; yellow solid matter then began to separate. After cooling, the crude 10-chloro-5:10-dihydrophenarsazine (8·6 g.) was filtered off and extracted with carbon tetrachloride. This solution, on cooling, deposited yellow needles, melting at 191—192° alone or mixed with an authentic sample of 10-chloro-5:10-dihydrophenarsazine.

Reduction of 2-Bromo-6′-aminodiphenylarsinic Acid. Isolation of o-Bromophenylarsenious Chloride.—A hot solution of 2-bromo-6′-aminodiphenylarsinic acid (5 g.) in alcohol (5 c.c.), concentrated hydrochloric acid (5 c.c.), and a trace of iodine was treated with sulphur dioxide for 45 minutes. On cooling, a gummy solid separated which slowly solidified. It was filtered off, and found to be *o*-bromophenylarsenious chloride, m. p. 65—66°, the melting point being unchanged by admixture with an authentic sample. 2-Bromo-6′-methylaminodiphenylarsinic acid and 2-bromo-6′-dimethylaminodiphenylarsinic acid under similar conditions yield methylaniline and dimethylaniline, identified as acetomethylanilide and *p*-nitrosodimethylaniline, respectively, together with *o*-bromophenylarsenious chloride.

Attempted Preparation of N-*Methylphenarsazinic Acid* (VII).—A mixture of 2-bromo-6′-methylaminodiphenylarsinic acid (11·1 g.), dry potassium carbonate (4·2 g.), amyl alcohol (80 c.c.), and a trace of copper powder was boiled under reflux for 12 hours. After steam distillation of the volatile products the aqueous residue was acidified and the crude acid (6·5 g.) filtered off. This was dissolved in alcoholic hydrochloric acid, and the boiling solution, to which a trace of iodine had been added, was saturated with sulphur dioxide for 20 minutes. A tarry precipitate was obtained which on extraction with carbon tetrachloride gave a crop of yellow needles, m. p. 191°. This substance was 10-chloro-5 : 10-dihydrophenarsazine, identified by comparison with an authentic sample.

The mother-liquors from the alcoholic hydrochloric acid treatment were evaporated, made alkaline with ammonia, and extracted with ether. This ethereal extract on evaporation gave a small quantity of an oil, smelling of methylaniline. On acetylation a small amount of acetomethylanilide, m. p. 101°, was obtained.

Action of Arsenious Chloride on Methyldiphenylamine.—(*a*) Attempts to prepare 10-chloro-5-methyl-5 : 10-dihydrophenarsazine from methyldiphenylamine and arsenious chloride in the presence of dichlorobenzene resulted in decomposition of the reacting substances and no crystalline matter could be isolated.

(*b*) Methyldiphenylamine (36·6 g.) and arsenious chloride (36·2 g.) were heated under reflux at 200° for 2 hours. The coloured residue was cooled, extracted with light petroleum, and the solid residue (46·2 g.) worked up, following as closely as possible the details described by Wieland and Rheinheimer (*loc. cit.*). The only compound isolated (yield 10%) was 10-chloro-5 : 10-dihydrophenarsazine, m. p. 187—190°, identical in every respect with an authentic specimen.

10-*Chloro*-5 : 10-*dihydrophenarsazine.*—A mixture of diphenyl-

amine (17 g.), arsenious chloride (20 g.), and *o*-dichlorobenzene (40 c.c.) was boiled under reflux for 5 hours, hydrogen chloride escaping steadily. On cooling, the dark green solution deposited a mass of crystals which were filtered off, washed with petrol, dried, and crystallised from carbon tetrachloride. 10-Chloro-5 : 10-dihydrophenarsazine prepared in this way melts at 191—192° and is bright yellow (yield almost theoretical).

The Reaction between Diphenylamine and Arsenious Chloride at the Ordinary Temperature.—Arsenious chloride (8·3 g.) was dissolved in dry benzene (10 c.c.) and treated with diphenylamine (7·8 g.). Solution resulted, and after 1 hour crystallisation commenced. After 24 hours the crystalline matter was filtered off rapidly in the absence of air, washed with dry benzene, and dried on porous tile in a vacuum (Found : Cl, 35·9. $C_{12}H_{12}NCl_4As$ requires Cl, 36·7%).

The crystals formed above, on filtration in the ordinary manner, become opaque and then consist for the most part of diphenylamine hydrochloride. The same compound is produced when diphenylamine hydrochloride and arsenious chloride are mixed in the presence of a solvent.

In an experiment using arsenious chloride (20 g.), diphenylamine (17 g.) and *s*-tetrachloroethane (40 c.c.), the mixture was kept for 16 months. No change of pressure in the flask was observed. After making alkaline with sodium carbonate solution, the volatile products were distilled in steam. The residue (3·0 g.) was converted into 10-chloro-5 : 10-dihydrophenarsazine by treating it in hot acetic acid solution with dry hydrogen chloride. On cooling, the chloroarsine separated in greenish-yellow needles, m. p. 189—190°.

p-*Phenylacetylaminophenylarsinic Acid* (N-*Acetyldiphenylamine*-p-*arsinic acid*) (X).—A solution of *N*-acetyl-*p*-aminodiphenylamine (22·6 g.) in dilute hydrochloric acid (25 c.c. of concentrated acid and 150 c.c. of water) was cooled to 0° and diazotised with sodium nitrite (7·4 g.) in water (20 c.c.). The diazo-solution was added gradually, with vigorous stirring, to a solution of sodium arsenite made by dissolving arsenious oxide (15 g.) in sodium carbonate solution (24 g. of anhydrous sodium carbonate in 105 c.c. of water) containing a small amount of copper sulphate. The arsenite solution was maintained at 30—35° and kept alkaline by addition of sodium hydroxide solution. After the evolution of nitrogen had ceased, the solution was filtered from tarry matter and made slightly acid to litmus. This procedure caused a further quantity of dark-coloured, tarry matter to be precipitated. After filtration, and evaporation to small bulk, the crude acid (16·5 g.), m. p. 121°, was obtained by making the solution strongly acid. The pure acid, m. p. 126° (decomp.), crystallises from water in almost colour-

less prisms containing $1H_2O$ (Found: H_2O, 4·7; As, 21·2. $C_{14}H_{16}O_5NAs$ requires H_2O, 5·1; As, 21·2%).

p-*Phenylaminophenylarsinic Acid* (*Diphenylamine*-p-*arsinic acid*) (XII).—The crude acetyl-arsinic acid (15 g.) was boiled for one hour with a mixture of concentrated hydrochloric acid (30 c.c.) and alcohol (30 c.c.). The solution turned green and the required arsinic acid was precipitated by water. The crude acid (13 g.) contained some green matter very difficult to separate. Purification was conveniently accomplished by treating a concentrated solution of the ammonium salt with magnesium sulphate solution, when the sparingly soluble magnesium salt was precipitated. Extraction of the magnesium salt with successive quantities of hot water and treatment of the solution with dilute sulphuric acid resulted in the formation of almost colourless, hair-like crystals of the arsinic acid, m. p. 265° (decomp.) (Found: As, 25·5. $C_{12}H_{12}O_3NAs$ requires As, 25·6%).

p-*Phenylacetylaminophenylarsenious Chloride* (*N-Acetyldiphenylamine*-p-*arsenious chloride*) (XI).—A hot solution of the acetylarsinic acid (9 g.) in alcohol (30 c.c.) and concentrated hydrochloric acid (9 c.c.) containing a trace of iodine was saturated with sulphur dioxide. On cooling, solid matter separated, and the mother-liquors on evaporation yielded a further crop of crystals. The *arsenious chloride*, after filtration and drying, crystallised from benzene–ligroin in colourless needles, m. p. 141° (Found: Cl, 20·0. $C_{14}H_{12}ONCl_2As$ requires Cl, 20·0%).

Considerable difficulty has been met with in trying to prepare the arsenious chloride from *p*-phenylaminophenylarsinic acid. Attempts at reduction analogous to those of the corresponding acetyl derivative using the crude acid were unsuccessful owing to the persistence of the green matter. An attempt at reduction in the absence of hydrochloric acid to produce the oxide, caused elimination of the arsenic and diphenylamine was obtained, identified by its melting point and the melting point of its hydrochloride. The pure acid on reduction in the presence of hydrochloric acid gave a crystalline product which was mainly diphenylamine hydrochloride. The crystals did contain a small amount of a substance containing arsenic, but not in sufficient quantity for identification.

Action of Arsenious Chloride on Aniline.—Aniline (51 g.) was added carefully to arsenious chloride (18 g.), and the mixture boiled gently for 72 hours. During the heating a sublimate of aniline hydrochloride and ammonium chloride formed. The product was made alkaline with sodium hydroxide solution and steam-distilled until the distillate was free from aniline and ammonia. By continued steam distillation, diphenylamine, identified by its melting point and the melting point of its hydrochloride, was obtained.

The insoluble residue in the flask was filtered, washed with water, dried at 100°, and weighed (39% of theory). The crude oxy-compound was converted into 10-chloro-5 : 10-dihydrophenarsazine by hydrochloric acid and acetone, and subsequent evaporation of the solution to dryness. The crude chloro-compound on crystallisation from carbon tetrachloride melted at 186—187°.

Action of Arsenious Chloride on β-Naphthylamine.—A mixture of β-naphthylamine (21·5 g.), arsenious chloride (30 g.), and *o*-dichlorobenzene (60 c.c.) was boiled under reflux for 18 hours. On mixing, a colourless, crystalline compound separated, which on warming dissolved. Hydrogen chloride was evolved and a white solid (ammonium chloride) collected in the condenser. The solution, on cooling, deposited a dark orange, crystalline mass. This was purified by three crystallisations from nitrobenzene and was thus obtained in yellow needles, m. p. 355° (decomp.) (Found : As, 19·3; N, 3·9. $C_{20}H_{13}NClAs$ requires As, 19·85; N, 3·7%).

14-*Chloro*-14 : 7-*dihydrodibenzophenarsazine* (XIV).—Di-β-naphthylamine (13·5 g.), arsenious chloride (10 g.), and *s*-tetrachloroethane (70 c.c.) were boiled under reflux for 90 minutes. After the first 30 minutes the yellow product began to separate from the boiling solution. The compound was filtered off and crystallised from nitrobenzene, separating in yellow needles, m. p. 355° (decomp.). The yield was 55% of the theoretical (Found : As, 19·6; N, 3·9. $C_{20}H_{13}NClAs$ requires As, 19·85; N, 3·7%).

7-*Chloro*-7 : 14-*dihydrodibenzophenarsazine* (XV).—Di-α-naphthylamine (13·5 g.; 1 mol.) and 10 g. of arsenious chloride (1·1 mols.) were boiled in 20 c.c. of *s*-tetrachloroethane for 7 hours. Hydrogen chloride escaped rather more slowly than in the previous preparations. The product separated, on cooling, as a brown powder (11·4 g., or 60·3%).

7-Chloro-7 : 14-dihydrodibenzophenarsazine crystallises from hot nitrobenzene in minute, yellowish-brown needles, m. p. 278—279° (decomp.) (Found : As, 19·6. $C_{20}H_{13}NClAs$ requires As, 19·85%).

10 : 10′-*Oxy*-5 : 10-*dihydrophenarsazine.*—A mixture of diphenylamine (15 g.), arsenious oxide (2·9 g.), and phosphorus pentoxide (3·2 g.) is heated with vigorous mechanical stirring at 160—170° for 1 hour. On cooling, a hard, black cake is obtained which is treated with sodium carbonate solution, and steam-distilled, diphenylamine (10·7 g.) passing over. The remaining oxy-compound (5 g.) is filtered off, and converted into 10-chloro-5 : 10-dihydrophenarsazine by dissolving it in acetone by addition of sufficient hydrochloric acid and evaporating the resulting solution to dryness. Crystallisation from carbon tetrachloride gives the pure product.

A mixture of 10 : 10′-oxy-5 : 10-dihydrophenarsazine (10 g.),

acetyl chloride (3·2 g.) and dry benzene (100 c.c.) is boiled under reflux for 6 hours, solution occurring after a few minutes' heating; on cooling, crystalline matter separates. This is filtered off and on washing with cold acetone yields crude 10-chloro-5-acetyl-5 : 10-dihydrophenarsazine (3·5 g.), m. p. 221—224°. By crystallisation from benzene, the pure product is readily obtained (compare Burton and Gibson, *loc. cit.*).

If 10 : 10′-oxy-5 : 10-dihydrophenarsazine (19·1 g.) is treated with benzoyl chloride (10·7 g.; 2 mols.) under similar conditions, no 10-chloro-5-benzoyl-5 : 10-dihydrophenarsazine is produced, but 10-chloro-5 : 10-dihydrophenarsazine (20·5 g.; theory, 21·2 g.), m. p. 190—191°, and benzoic anhydride (7·9 g.; theory, 8·6 g.), m. p. 41°, are obtained.

Molecular Compounds of 10-*Chloro*-5 : 10-*dihydrophenarsazine.*—When 10-chloro-5 : 10-dihydrophenarsazine is crystallised from the following solvents, crystals are obtained containing solvent of crystallisation. These crystals effloresce slowly in air, but heating at 110° causes rapid dissociation, leaving pure 10-chloro-5 : 10-dihydrophenarsazine in each case.

(*a*) Acetic acid	$A,C_2H_4O_2$	(Loss, 18·5; calc., 17·8%)
(*b*) *s*-Tetrachloroethane	$2A,C_2H_2Cl_4$	(,, 23·7; ,, 23·2)
(*c*) Chlorobenzene	$2A,C_6H_5Cl$	(,, 17·0; ,, 16·8)
(*d*) *o*-Dichlorobenzene	$2A,C_6H_4Cl_2$	(,, 21·0; ,, 20·9)
(*e*) Acetone	$2A,C_3H_6O$	(,, 9·3; ,, 9·5)
(*f*) Carbon tetrachloride	A,CCl_4	(,, 35·6; ,, 35·7)

(A denotes $NH<^{C_6H_4}_{C_6H_4}>AsCl$).

10-Chloro-5 : 10-dihydrophenarsazine is extremely soluble in arsenious chloride, giving a dark green solution. A hot, concentrated solution, on cooling, deposits magnificent, scarlet scales of the compound $A,AsCl_3$ (loss, 39·3; calc., 39·7%). This is sufficiently stable to allow of filtration, but on exposure to air or washing with solvents yields the original chloro-compound.

10-*Bromo*-5 : 10-*dihydrophenarsazine.*—(*a*) A mixture of diphenylamine (8·5 g.), arsenious bromide (17·3 g.), and *o*-dichlorobenzene (20 c.c.) is boiled under reflux for 18 hours. Hydrogen bromide is liberated steadily. The crude bromo-compound (9·6 g.) that separates on cooling crystallises from toluene in greenish-yellow prisms, m. p. 217—218°.

(*b*) 10-Acetyl-5 : 10-dihydrophenarsazine (15 g.) dissolved in boiling glacial acetic acid (200 c.c.) is treated with hydrobromic acid (10 c.c.; 30%) in glacial acetic acid (25 c.c.). On cooling, 10-bromo-5 : 10-dihydrophenarsazine (13·3 g.) separates (Found : As, 23·3; Br, 24·8%).

10-*Iodo*-5 : 10-*dihydrophenarsazine.*—On treating a hot solution

of 10-acetyl-5 : 10-dihydrophenarsazine (4·5 g.) in glacial acetic acid (70 c.c.) with hydriodic acid (2·5 c.c.; 50%) diluted with acetic acid (10 c.c.) the pure iodo-compound (5·6 g.) separates in brownish-orange needles, m. p. 217—221° (decomp.) (Found: As, 20·1%).

10-n-*Butoxy*-5 : 10-*dihydrophenarsazine*, $NH(C_6H_4)_2As{\cdot}O{\cdot}C_4H_9$.—A solution of 10 : 10′-oxy-5 : 10-dihydrophenarsazine (5 g.) in *n*-butyl alcohol (50 c.c.), on cooling deposited a mass of pale yellow needles, m. p. 158—160° (Found: As, 23·7. $C_{16}H_{18}ONAs$ requires As, 23·8%).

A boiling solution of 10 : 10′-oxy-5 : 10-dihydrophenarsazine (15 g.) in *n*-butyl alcohol (180 c.c.) is saturated with dry hydrogen sulphide for 2 hours. The compound crystallises during the reaction and after collection is recrystallised from toluene. 10 : 10′-Sulpho-5 : 10-dihydrophenarsazine crystallises in yellow needles, m. p. 256—264° (decomp.). Yield 67% of theory (Found: As, 29·1%).

10-*Benzyloxy*-5 : 10-*dihydrophenarsazine*,

$$NH(C_6H_4)_2AsO{\cdot}CH_2{\cdot}C_6H_5,$$

prepared in an analogous manner to the corresponding *n*-butyl compound, crystallises in colourless needles, m. p. 173—175° (Found: As, 21·1. $C_{19}H_{16}ONAs$ requires As, 21·5%).

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LIX.—10-*Chloro*-5 : 10-*dihydrophenarsazine and its Derivatives. Part II. The Action of Primary Chloroarsines on Diphenylamine and its Homologues.*

By HAROLD BURTON and CHARLES STANLEY GIBSON.

IT has been shown (preceding paper) that the reaction between arsenious chloride and diphenylamine and its homologues goes very readily either when the two substances are heated alone, or more conveniently, in the presence of a suitable solvent, dihydrophenarsazine derivatives being formed. The reaction taking place may be generally expressed ($R_1 = R - H$; $R'_1 = R' - H$):

$$AsCl_3 + HN{\cdot}RR' \longrightarrow 2HCl + ClAs\langle{}^{R_1}_{R'_1}\rangle NH.$$

It seemed desirable to investigate the application of the reaction to the case of dichloroarsines with a view to obtain dihydrophenarsazine derivatives of the type $XAs\langle{}^{R_1}_{R'_1}\rangle NH$ [X = univalent hydrocarbon or substituted hydrocarbon radical]. The most

convenient dichloroarsine was phenyldichloroarsine, easily prepared by reducing phenylarsinic acid, which in turn is readily obtainable by the Bart reaction on aniline.

When the reaction between phenyldichloroarsine and diphenylamine was carried out under the conditions employed for preparing 10-chloro-5 : 10-dihydrophenarsazine, *viz.*, with equimolecular quantities heated in the presence of *o*-dichlorobenzene, the product was not 10-phenyl-5 : 10-dihydrophenarsazine, but 10-chloro-5 : 10-dihydrophenarsazine, the substance obtained by the condensation of arsenious chloride and diphenylamine. It appeared that the reaction to produce 10-chloro-5 : 10-dihydrophenarsazine might be either (*a*) or (*b*).

(*a*) $AsPhCl_2 + NHPh_2 \longrightarrow ClAs\langle{}^{C_6H_4}_{C_6H_4}\rangle NH + C_6H_6 + HCl.$

(*b*) $2AsPhCl_2 + NHPh_2 \longrightarrow ClAs\langle{}^{C_6H_4}_{C_6H_4}\rangle NH + AsPh_2Cl + 2HCl.$

It was also recognised that reaction (*a*) might be the final result of the following two reactions.

(i) $AsPhCl_2 + NHPh_2 \longrightarrow PhAs\langle{}^{C_6H_4}_{C_6H_4}\rangle NH + 2HCl.$

(ii) $PhAs\langle{}^{C_6H_4}_{C_6H_4}\rangle NH + HCl \longrightarrow ClAs\langle{}^{C_6H_4}_{C_6H_4}\rangle NH + C_6H_6.$

In a preliminary experiment two molecules of the chloroarsine and one molecule of diphenylamine were heated together in *o*-dichlorobenzene solution. A theoretical yield of 10-chloro-5 : 10-dihydrophenarsazine calculated on the quantity of diphenylamine taken was obtained, and instead of the easily recognisable diphenylchloroarsine, only phenyldichloroarsine was obtained on examining the filtrate from the solid product. Experiments using molecular proportions of the reacting substances, heated for a longer time, also gave theoretical amounts of 10-chloro-5 : 10-dihydrophenarsazine, but it was not until the reaction was carried out in the absence of solvent that we were able to collect a volatile substance, which was identified as benzene.

In view of these results, the publication of a paper by Lewis and Stiegler (*J. Amer. Chem. Soc.*, 1925, **47**, 2551) containing experiments on the condensation of β-chlorovinyldichloroarsine with diphenylamine and phenyl-α-naphthylamine, and the description of the condensation products "6-β-chlorovinylphenarsazine," and "7-β-chlorovinyl-7 : 12-dihydro-γ-benzophenarsazine," seemed somewhat anomalous to us, especially as the melting points of the two compounds quoted (186—187° and 213°, respectively) were so near to those of 10-chloro-5 : 10-dihydrophenarsazine and 7-chloro-

7 : 12-dihydrobenzophenarsazine (191—192° and 219—220°, respectively), and therefore we decided to repeat our work; extend it to other diarylamines; and finally repeat Lewis and Stiegler's experiments.

We have done this and find that our initial observations are correct. The extension of the work consisted in studying the action of phenyldichloroarsine on phenyl-*p*-tolylamine, *pp'*-ditolylamine, and phenyl-α-naphthylamine. In each case, the reaction proceeded as with diphenylamine and instead of the *As*-phenyl derivatives we obtained the chlorodihydrophenarsazine derivative.

The compound isolated from phenyl-*p*-tolylamine, namely, 10-*chloro*-2-*methyl*-5 : 10-*dihydrophenarsazine*,* has been synthesised from the former substance and arsenious chloride. The *N*-acetyl derivative of this compound has been prepared, and also the corresponding *phenarsazinic acids*, using the method of Burton and Gibson (J., 1924, **125**, 2276). The compound obtained from *pp'*-ditolylamine is referred to in the German Patent (D.R.-P. 281049, Friedländer, "Fortschritte," 1914, XII, 843), but so far as we can discover, this substance, 10-*chloro*-2 : 8-*dimethyl*-5 : 10-*dihydrophenarsazine*, has not yet been described in the literature. We have prepared it from *pp'*-ditolylamine and arsenious chloride, and also obtained its N-*acetyl* derivative.

A repetition of Lewis and Stiegler's work, adhering as far as possible to their quantities and conditions, showed that the reaction between diphenylamine and β-chlorovinyldichloroarsine proceeded in a similar manner to that using phenyldichloroarsine. In the presence of *o*-dichlorobenzene a quantitative yield of 10-chloro-5 : 10-dihydrophenarsazine was obtained, which after crystallisation from carbon tetrachloride melted at 186—187° and did not depress the melting point of a pure specimen. Further crystallisation from the same solvent gave a pure product, m. p. 190—191°, identical with an authentic specimen. From phenyl-α-naphthylamine in boiling *o*-dichlorobenzene solution we isolated 7-chloro-7 : 12-dihydrobenzophenarsazine, also in quantitative yield. In the absence of solvent, the yields were not so good, but the products obtained were identical with those from the experiments done in *o*-dichlorobenzene. It was found necessary to crystallise the crude 10-chloro-5 : 10-dihydrophenarsazine twice from carbon tetrachloride before it would melt at 190—191°, and although the product from phenyl-α-naphthylamine was crystallised from xylene, following Lewis and Stiegler's directions, it melted three degrees low, and had to be further crystallised from toluene before it was pure. We were able

* The nomenclature of these compounds is described in the preceding paper.

to prove the formation of vinyl chloride in these experiments by passing the hydrogen chloride and vinyl chloride evolved through a solution of bromine in carbon tetrachloride, when the colour of the bromine was discharged. That this decoloration was not due to acetylene produced by decomposition of the β-chlorovinyldichloroarsine was further demonstrated by washing the carbon tetrachloride solution with dilute sodium carbonate solution, and after subsequent drying and removal of the carbon tetrachloride, determining the boiling point of the residue. This was 160—162°, which is in good agreement with the b. p., 162·5—163°, recorded by Biltz (*Ber.*, 1902, **35**, 3526) for α-bromo-β-chlorobromoethane.* During these experiments we were unable to isolate any compound of the type $XAs<^{R_1}_{R'_1}>NH$.

Experimental.

Freshly-made phenyldichloroarsine, b. p. 247—250°/752 mm., and β-chlorovinyldichloroarsine, b. p. 93—94°/24 mm., were used in the following experiments. The diphenylamine and *o*-dichlorobenzene also were freshly distilled.

Condensations of Phenyldichloroarsine with Diphenylamine and Related Compounds.—(a) *In the presence of solvent.* In the preliminary experiments a mixture of diphenylamine (8·45 g.), phenyldichloroarsine (22·3 g.), and *o*-dichlorobenzene (20 c.c.) was heated under reflux for 8 hours. Hydrogen chloride had then ceased to be evolved. The green solution was cooled, mixed with petrol (20 c.c.), and the solid filtered off. This, after being washed with petrol (30 c.c.) and dried to constant weight at 100°, crystallised from benzene in yellow needles, m. p. 189—190°, and was identical in all respects with an authentic sample of 10-chloro-5 : 10-dihydrophenarsazine prepared from diphenylamine and arsenious chloride. The yield was almost theoretical.

Similar experiments using (*a*) phenyl-*p*-tolylamine, (*b*) di-*p*-tolylamine, and (*c*) phenyl-α-naphthylamine gave (*a*) 10-*chloro*-2-*methyl*-5 : 10-*dihydrophenarsazine*, m. p. 199—200° (decomp.), (*b*) 10-*chloro*-2 : 8-*dimethyl*-5 : 10-*dihydrophenarsazine*, m. p. 261—262°, after

* Lewis and Stiegler, in calculating the value for the percentage of chlorine in the supposed 10-β-chlorovinyl-5 : 10-dihydrophenarsazine, arrived at too high a value, the actual figure being 11·69% instead of 12·00%. Their low analytical data for a sample of pure 10-chloro-5 : 10-dihydrophenarsazine together with its low melting point explain, in all probability, the reason they have assigned the wrong constitution to this compound. The obvious impurity of their 7-chloro-7 : 12-dihydrobenzophenarsazine, the m. p. of which was 6° below that of a pure specimen, is, no doubt, the cause of their low analytical data.

previous decomposition, and (*c*) 7-chloro-7:12-dihydrobenzophenarsazine, m. p. 218—219°.

In the second series of experiments, half the quantity of phenyldichloroarsine was used and the mixture was boiled for 16 hours. The product was treated in the same manner, and a yield of 93% of the theoretical quantity of 10-chloro-5:10-dihydrophenarsazine was obtained. (The yields of the other chlorodihydrophenarsazines varied from 90—95%.)

(b) *In the absence of solvent.* These experiments consisted in heating mixtures of diphenylamine and phenyldichloroarsine, in the molecular ratio of 1:1 and 1:2, in a metal-bath, the temperature of which was raised to 230° during 30 minutes and maintained for 45 minutes. The volatile product, after being washed with dilute sodium carbonate solution and dried, boiled at 80°; it was benzene. The residue in the flask, after crystallising from boiling *o*-dichlorobenzene, was 10-chloro-5:10-dihydrophenarsazine.

10-*Chloro*-2-*methyl*-5:10-*dihydrophenarsazine*,

$$ClAs\begin{<}C_6H_3Me\\C_6H_4\end{>}NH.$$

—A mixture of phenyl-*p*-tolylamine (36·6 g.), arsenious chloride (40 g.), and *o*-dichlorobenzene (80 c.c.) was boiled under reflux for 4 hours. On cooling, the chloro-compound (51 g.) separated as a mass of green crystals. On crystallisation from benzene, the substance was obtained in yellow needles, m. p. 199—200° (decomp.) (Found: Cl, 12·3. $C_{13}H_{11}NClAs$ requires Cl, 12·2%).

10-*Chloro*-2:8-*dimethyl*-5:10-*dihydrophenarsazine*,

$$ClAs(C_6H_3Me)_2NH,$$

was prepared by heating together for 4 hours a mixture of di-*p*-tolylamine (32·7 g.), arsenious chloride (33·2 g.), and *o*-dichlorobenzene (133 c.c.). The crude chloro-compound (44·7 g.) crystallised from nitrobenzene in orange prisms, m. p. 261—262° with previous decomposition (compare D.R.-P., *loc. cit.*) (Found: As, 24·2. $C_{14}H_{13}NClAs$ requires As, 24·5%).

10-*Chloro*-5-*acetyl*-2-*methyl*-5:10-*dihydrophenarsazine* was prepared by boiling a mixture of the corresponding phenarsazine (30 g.) with acetic anhydride (60 c.c.) for 3½ hours. On cooling, the *acetyl* derivative (25 g.) separated in almost colourless crystals. It separated from benzene–light petroleum in clusters of almost colourless needles, m. p. 154—155° (Found: Cl, 10·7. $C_{15}H_{13}ONClAs$ requires Cl, 10·6%).

10-*Chloro*-5-*acetyl*-2:8-*dimethyl*-5:10-*dihydrophenarsazine*.—A suspension of the chloroarsine (10 g.) in acetic anhydride (50 c.c.) was boiled for 2 hours, when solution was complete and the colour of

the original compound had almost disappeared. After removal of half the acetic anhydride by distillation the crude acetyl compound separated in nearly colourless needles. It separated from benzene–light petroleum in colourless needles, m. p. 164—165° (Found: As, 21·4. $C_{16}H_{15}ONClAs$ requires As, 21·6%).

2-*Methylphenarsazinic acid*, $NH<^{C_6H_3Me}_{C_6H_4}>AsO\cdot OH$, separated in good yield when a mixture of the chloroarsine and chloramine-T had stood for 12 hours. It crystallised from aqueous acetic acid in colourless, fine needles which did not melt when heated but decomposed above 300° (Found: As, 25·6. $C_{13}H_{12}O_2NAs$ requires As, 25·9%). The *sodium* salt crystallises from water in colourless, hair-like needles. The *hydrochloride* was obtained by treating a suspension of the acid in boiling alcohol with concentrated hydrochloric acid until crystalline matter began to separate. On cooling, the hydrochloride separated in colourless, small prisms, m. p. 209—211° (decomp.) (Found: Cl, 10·9. $C_{13}H_{12}O_2NAs,HCl$ requires Cl, 10·9%).

2 : 8-*Dimethylphenarsazinic acid* was prepared by boiling a suspension of the chloroarsine (10 g.) in acetone (200 c.c.) with a solution of chloramine-T (18·5 g. in 185 c.c. of water) for 30 minutes. The orange colour of the original substance disappeared and colourless, crystalline matter was produced. The *acid* (6·3 g.) separated from aqueous acetic acid in colourless, glistening plates, which decomposed without melting at a high temperature (Found: As, 24·5. $C_{14}H_{14}O_2NAs$ requires As, 24·7%). The *sodium* salt crystallises from water in colourless needles, and the *hydrochloride*, prepared as above, was obtained in colourless needles, m. p. 216° (decomp.) after previous softening (Found: As, 21·7. $C_{14}H_{14}O_2NAs,HCl$ requires As, 22·1%).

N-*Acetyl*-2 : 8-*dimethylphenarsazinic acid*, prepared in the usual manner, separated from dilute acetic acid in colourless prisms, m. p. 240° (decomp.) (Found: As, 21·65. $C_{16}H_{16}O_3NAs$ requires As, 21·7%).

Condensation of β-*Chlorovinyldichloroarsine with Diphenylamine and Phenyl-*α-*naphthylamine.*—(a) *In the presence of solvent.* The mixture of diphenylamine (10·6 g.), β-chlorovinyldichloroarsine (13·0 g.), and *o*-dichlorobenzene (25 c.c.) was boiled under reflux for 12 hours. Owing to the formation of a certain amount of tarry matter, the crude compound, isolated as in the phenyldichloroarsine experiments, was extracted in a Soxhlet with carbon tetrachloride. The 10-chloro-5 : 10-dihydrophenarsazine obtained melted at 187° without further crystallisation, and a sample of it did not depress

the melting point of an authentic specimen. The yield was quantitative. Further crystallisation from the same solvent gave pure 10-chloro-5 : 10-dihydrophenarsazine, m. p. 190—191°. A similar experiment using phenyl-α-naphthylamine gave 7-chloro-7 : 12-dihydrobenzophenarsazine, m. p. 218—219°.

(b) *In the absence of solvent.* The quantities and conditions used in these experiments were the same as those described by Lewis and Stiegler. The only difference in procedure after the initial reaction was that the crude mass from the diphenylamine was extracted with carbon tetrachloride in a Soxhlet apparatus and finally crystallised from carbon tetrachloride. In this way, we obtained a specimen of pure 10-chloro-5 : 10-dihydrophenarsazine, m. p. 190—191° (Found : Cl, 12·8; As, 26·8%). From the phenyl-α-naphthylamine experiment pure 7-chloro-7 : 12-dihydrobenzophenarsazine was obtained, m. p. 219—220° (compare Lewis and Hamilton, *J. Amer. Chem. Soc.*, 1921, **43**, 2218) after a further crystallisation from toluene (Found : Cl, 10·9%).

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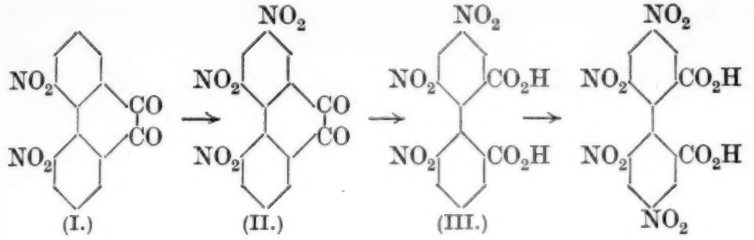
LX.—*The Molecular Configurations of Polynuclear Aromatic Compounds. Part V. The Identity of the Nitration Products derived from* 2 : 7- *and* 4 : 5-*Dinitrophenanthraquinones.*

By GEORGE HALLATT CHRISTIE and JAMES KENNER.

THE conversion of 2 : 7-dinitrophenanthraquinone successively into 2 : 4 : 7-trinitrophenanthraquinone and 4 : 6 : 4′-trinitrodiphenic acid,

$$C_{12}H_6(NO_2)_2\langle\begin{matrix}CO\\CO\end{matrix} \longrightarrow C_{12}H_5(NO_2)_3\langle\begin{matrix}CO\\CO\end{matrix} \longrightarrow C_{12}H_5(NO_2)_3(CO_2H)_2,$$

has been already described (Christie and Kenner, J., 1923, **123**, 779). At the same time, it was intimated that a similar set of reactions had been carried out in the case of the dinitro-quinone which is produced with the 2 : 7-isomeride by nitration of phenanthraquinone and which Schmidt and Kämpf (*Ber.*, 1903, **36**, 3745) concluded to be a 4 : 5-derivative (I). The new trinitroquinone was therefore thought to be a 2 : 4 : 5-derivative (II), and so different from the above-mentioned 2 : 4 : 7-isomeride, when it was oxidised to a diphenic acid (III) from which 4 : 6 : 4′ : 6′-tetranitrodiphenic acid was obtained by further nitration :



It was therefore remarkable that when the acid (III) was resolved into optically active forms by fractional crystallisation of the quinidine or, better, of the quinine salts, a very close correspondence was revealed between the physical constants of the various salts and of those derived from the 4 : 6 : 4′-trinitro-acid. This will be apparent from the following table :

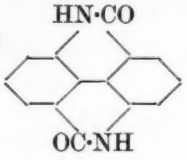
	4 : 6 : 4′-Acid.	New acid.
Melting point.	289—290°	291°
Quinine *d*-salt.	M. p. 222°; $[\alpha]_D$ −156·4°	M. p. 222°; $[\alpha]_D$ −156·1°
„ *l*-salt.	M. p. 175°; $[\alpha]_D$ − 69·1°	M. p. 176°; $[\alpha]_D$ − 77·5°
Quinidine *l*-salt.	M. p. 229°; $[\alpha]_D$ −191·1°	M. p. 228°; $[\alpha]_D$ −189·2°
„ *d*-salt.	M. p. 176°; $[\alpha]_D$ 85·5°	M. p. 178°; $[\alpha]_D$ 109·9°
Sodium salt, *d*-acid.	$[\alpha]_D$ −152·3°	$[\alpha]_D$ −151·1°

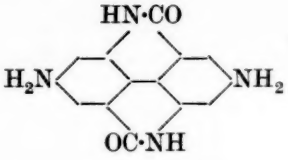
This agreement also extends to the original trinitro-quinones, each of which crystallises from benzene in yellow, hexagonal prisms, which melt at 209° and contain one molecular proportion of benzene of crystallisation.

In spite, therefore, of the apparently conclusive nature of the evidence in favour of the constitutional formulæ assigned to these various compounds, the possibility suggested itself that the two series might in reality be identical. This was confirmed when it was found that the melting point of the two acids was not depressed by mixing them, and that the same applied to the *quinoxaline* derivative, m. p. 307°, prepared by condensing each of the trinitro-quinones with *o*-phenylenediamine. It followed either that the orientation of the two dinitro-quinones, from which the same trinitro-quinone had been obtained, was in some respect faulty or that, in the course of nitration of these dinitro-compounds, migration of a nitro-group had occurred in one case. Whichever of these be correct, it seemed advisable if possible to determine the orientation of the trinitro-compound by an independent method.

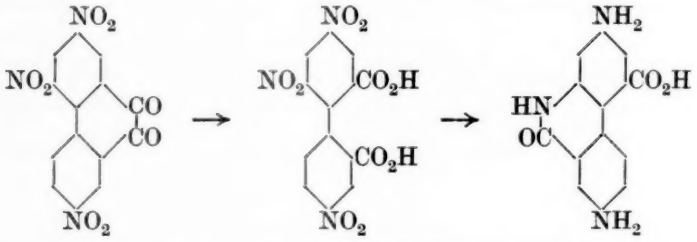
It had previously been shown (Kenner and Stubbings, J., 1921, **119**, 593) that γ-6 : 6′-dinitrodiphenic acid was converted by reduction into a phenanthridone derivative (IV), and it was now found that 4 : 6 : 4′ : 6′-tetranitrodiphenic acid is similarly convertible

into the corresponding diamino-compound (V), of which both neutral and basic sulphates were isolated.

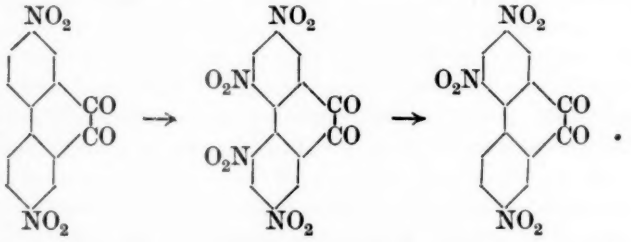
(IV.) 

 (V.)

The trinitrodiphenic acid, however, under similar conditions yielded an amino-acid soluble both in alkali and in excess of mineral acid. Clearly this result indicates that the trinitro-acid is a 4 : 6 : 4′-derivative, derived from a 2 : 4 : 7-trinitrophenanthraquinone :

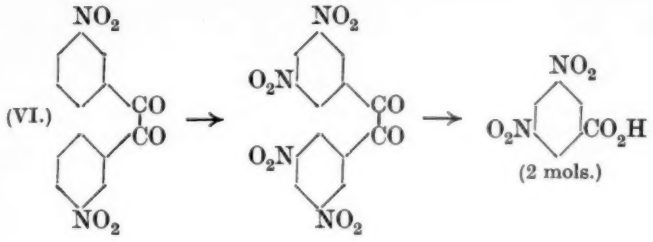


It has been pointed out (J., 1923, **123**, 780) that a 2 : 4 : 5 : 7-tetranitrophenanthraquinone could not be obtained from the trinitro-compound under very vigorous conditions of nitration. Hence it was just conceivable that the production of the same trinitro-compound from the two dinitrophenanthraquinones was due to the formation of the tetranitro-derivative in the first place, followed by elimination of a nitro-group under the conditions of experiment :

(I.) and 

Although this would be a novel reaction, and is not observed in the case of the compound 4 : 6 : 4′ : 6′-tetranitrodiphenic acid, it was deemed advisable to examine the behaviour of the closely related compound, 3 : 3′-dinitrobenzil (VI), on nitration. No difficulty was experienced in converting this into the corresponding

3 : 5 : 3′ : 5′-*tetranitrobenzil*, the constitution of which was proved by its oxidation to 3 : 5-dinitrobenzoic acid :



Experimental.

2 : 4 : 7-*Trinitrophenanthraquinone from* 4 : 5-*Dinitrophenanthraquinone*.—When the procedure described in the case of 2 : 7-dinitrophenanthraquinone (Christie and Kenner, *loc. cit.*, p. 783) was applied to the 4 : 5-isomeride, the trinitro-derivative was obtained, after crystallisation from benzene, in stout, yellow prisms, m. p. 209° (Found : loss of weight at 120°, 18·6. $C_{14}H_5O_8N_3,C_6H_6$ requires loss, 18·5%. Found for material previously heated at 120°. N, 12·3. $C_{14}H_5O_8N_3$ requires N, 12·25%). Solutions of the quinone (0·75 g.) and *o*-phenylenediamine (0·38 g.) in glacial acetic acid reacted at once when mixed. The precipitated *quinoxaline* derivative separated from benzene in clusters of colourless needles, m. p. 307° (Found : N, 16·75. $C_{20}H_9O_6N_5$ requires N, 16·9%). An identical product was obtained from the quinone derived from 2 : 7-dinitrophenanthraquinone.

4 : 6 : 4′-*Trinitrodiphenic Acid from* 4 : 5-*Dinitrophenanthraquinone*.—The acid prepared from the above trinitroquinone by the usual process of oxidation with potassium dichromate and sulphuric acid was obtained first as an oil and then as a solid, m. p. 292° [Found : equiv., 188·3. $C_{12}H_5O_6N_3(CO_2H)_2$ requires equiv., 188·5]. Solutions of the acid (4·6 g.) in alcohol (100 c.c.) and of quinine hydrate (9·2 g.) in alcohol (70 c.c.) were mixed and boiled; a salt (5·8 g.) separated on cooling. On evaporating the alcoholic liquor, an oil remained from which a second salt (5·8 g.) was obtained by treatment with dry ether.

Quinine d-4 : 6 : 4′-*trinitrodiphenate*, the less soluble of the two salts so obtained, forms colourless, octahedral prisms, m. p. 222·5° (decomp.) and free from alcohol. For a 1·25% solution in 10*N*-acetic acid, $[\alpha]_D^{19°} = -156·1°$ (Found : N, 9·6. $C_{54}H_{55}O_{14}N_7$ requires N, 9·6%).

Quinine l-4 : 6 : 4′-*trinitrodiphenate* melts at 176° (decomp.) after repeated purification by solution in alcohol and precipitation by

ether. For a 0·5% solution in chloroform, $[\alpha]_D^{19°} = -77·5°$ (Found: N, 9·7. $C_{54}H_{55}O_{14}N_7$ requires N, 9·6%).

Quinidine salts, m. p. 228° and 178°, agreeing in crystalline form with those previously described (Christie and Kenner, *loc. cit.*) were also obtained. For 0·7% solutions in chloroform, the respective observed values for $[\alpha]_D$ were $-189·2°$ and $+109·9°$. The poor agreement between the latter value and that previously recorded is to be attributed partly to a clerical error, which led to the value 56·04° being quoted in place of the correct value of 85·55°, and partly to the lower melting point of the salt employed on the previous occasion.

d-4 : 6 : 4′-Trinitrodiphenic acid, prepared from the quinine salt in the manner described in the earlier papers, was an oil which very slowly solidified to colourless prisms, m. p. 281—282° (decomp.). For a 3·11% solution in ether, $[\alpha]_D = +23·47°$, and on conversion into a 1·48% solution of the sodium salt, $[\alpha]_D = -149·0°$. For a 0·84% solution of sodium salt prepared without investigating the rotatory power of the acid, $[\alpha]_D = -151·1°$. For a 1·36% solution of the sodium salt from the quinidine salt, m. p. 178°, $[\alpha]_D = -146·1°$, and the acid melted at 281—282° (decomp.).

l-4 : 6 : 4′-Trinitrodiphenic acid, from the quinine salt, melted and decomposed at 280—282°, and showed $[\alpha]_D = -15·14°$ for a 2·80% solution in ether. For a 1·05% solution of the sodium salt subsequently prepared, $[\alpha]_D = +136·6°$. The changes in sign of rotatory power thus observed in passing from the acid to the sodium salt show that the prefixes *d*- and *l*- as used in the previous paper require to be interchanged.

Quinine salts prepared from the acid derived from 2 : 7-dinitrophenanthraquinone melted at 222° and 175°, respectively, and exhibited specific rotatory powers of $-156·4°$ (1·28% solution in 10*N*-acetic acid) and $-69·11°$ (0·63% solution in chloroform).

Reduction of 4 : 6 : 4′ : 6′-*Tetranitrodiphenic Acid.*—When a solution of stannous chloride (33 g.) in hydrochloric acid (30 c.c.) was slowly added to a solution of the acid (3 g.) in glacial acetic acid (30 c.c.) and hydrochloric acid (24 c.c.), heat was evolved, a red colour was produced which slowly disappeared, and a precipitate formed. This was collected after the mixture had been boiled for an hour, and after being washed with hydrochloric acid it was dissolved in concentrated sulphuric acid. By cautious dilution with water, yellow plates were obtained which turned green when exposed to the air and light, and left no residue on ignition. They blackened, but did not melt, when heated to 300° (Found: N, 15·2. $C_{14}H_{10}O_2N_4,H_2SO_4$ requires N, 15·4%). The aqueous extract obtained by warming the material with sodium carbonate

solution was shown in the usual manner to contain sulphate ions.

When a solution of the material in sulphuric acid was added to sodium acetate solution, a green precipitate was obtained which still contained sulphur after being thoroughly washed and was apparently a basic sulphate (Found : N, 17·7. $C_{14}H_{10}O_2N_4,\frac{1}{2}H_2SO_4$ requires N, 17·8%).

Reduction of 4 : 6 : 4′*-Trinitrodiphenic Acid.*—The result of applying the procedure described above to 4 : 6 : 4′-trinitrodiphenic acid was less satisfactory than that of heating a suspension of the finely ground acid in hydrochloric acid at 100° with an amount of tin about 50% in excess of that theoretically necessary for complete reduction. By collecting the almost colourless solid portion of the product, washing it with hydrochloric acid, and cautious precipitation with water of its solution in sulphuric acid, a yellow material was obtained which turned green on exposure to air and exhibited the properties of an amino-acid [Found : N, 11·3; equiv., 120·6. $C_{13}H_{10}ON_3(CO_2H),H_2SO_4$ requires N, 11·45%; equiv., 122·3].

3 : 5 : 3′ : 5′*-Tetranitrobenzil.*—Dinitrobenzil (30 g.) reacted vigorously with nitric acid (150 g.; *d* 1·5) and sulphuric acid (180 g.) when heated at 100° for 10 minutes, so that it was necessary to cool the liquid. Finally, the mixture was heated for 20 hours at 100° and then poured on to ice. The solid product consisted of 3 : 5-dinitrobenzoic acid (m. p. 205°, equiv. 213·1) and a neutral substance insoluble in cold sodium carbonate solution. By crystallisation from benzene, yellow needles of a tetranitrobenzil, m. p. 168°, were obtained (Found : N, 14·35. $C_{14}H_6O_{10}N_4$ requires N, 14·35%). Its orientation was demonstrated by adding excess of hydrogen peroxide to a solution of the compound in dilute aqueous sodium hydroxide. Heat was evolved and after about ½ hour the dark coloration first produced had given place to a pale yellow. An excellent yield of 3 : 5-dinitrobenzoic acid was obtained on acidification. Tetranitrobenzil was, however, unchanged by prolonged heating with the above nitration mixture, so that it was not an intermediate product in the formation of dinitrobenzoic acid from dinitrobenzil.

The *quinoxaline* derivative of tetranitrobenzil, prepared in the usual manner by condensation in glacial acetic acid solution, formed colourless needles, m. p. 274° (Found : N, 18·4. $C_{20}H_{10}O_8N_6$ requires N, 18·2%).

One of us (G. H. C.) wishes to make grateful acknowledgment of a grant from the Department of Scientific and Industrial Research

which enabled him to participate in this work. We are also indebted to the Research Fund Committee of the Chemical Society for a grant towards the purchase of materials.

THE UNIVERSITY, SHEFFIELD. [*Received, December 28th*, 1925.]

LXI.—*Orientation Effects in the Diphenyl Series. Part I.*

By HENRY GEORGE DENNETT and EUSTACE EBENEZER TURNER.

SINCE the nitration of 4 : 4′-dihydroxydiphenyl (Kunze, *Ber.*, 1888, **21**, 3331; Schultz, *ibid.*, 3530; Hirsch, *ibid.*, 1889, **22**, 336) and of its diethyl ether (Hirsch, *loc. cit.*; Brady and McHugh, J., 1923, **123**, 2047) affords symmetrical (3 : 5′-)dinitro-derivatives, it might be supposed that 4 : 4′-dibromodiphenyl would nitrate to give 4 : 4′-dibromo-3 : 5′(or 3 : 3′)-dinitrodiphenyl. Unsymmetrical nitration, however, actually occurs, with the almost quantitative formation of the 2 : 3′(2 : 5′ ?)-dinitro-compound. This is the first example of unsymmetrical substitution in the diphenyl series.

Whilst the nitration of *p*-tolyl ethyl ether apparently affords only the 3-nitro-derivative (Staedel, *Annalen*, 1883, **217**, 162), *p*-chlorotoluene yields a mixture of approximately equal quantities of the 2- and 3-nitro-compounds (Holleman, *Proc. K. Akad. Wetensch. Amsterdam*, 1908, **11**, 257).

The nitration of 4 : 4′-dibromodiphenyl was described by Fittig (*Annalen*, 1864, **132**, 206) and Schultz (*ibid.*, 1874, **174**, 218) as giving a dinitro-derivative, m. p. 148°, regarded by Beilstein (*Handbuch*, 4th Edn., v, 585) as probably being identical with the 2 : 2′-dinitro-compound, m. p. 138°, previously synthesised by Ullmann and Bielecki (*Ber.*, 1901, **34**, 2177). The work of Fittig and Schultz has been repeated and confirmed. Reduction of their dinitro-compound afforded the diamine, m. p. 89°, described by Schultz (*loc. cit.*), but this diamine could not be caused to undergo condensations of the type to be expected of a symmetrical diamine. This appeared to show that unsymmetrical nitration had occurred. Moreover, the dinitro-derivative depressed the m. p. of the 2 : 2′-dinitro-compound obtained from 2 : 5-dibromonitrobenzene (Ullmann and Bielecki, *loc. cit.*).

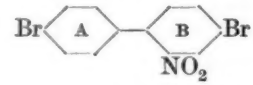
4 : 4′-*Dibromo*-2-*nitrodiphenyl*, prepared from 2-nitrobenzidine, was identical with the mononitro-derivative, m. p. 124°, prepared by Lellmann's method (*Ber.*, 1882, **15**, 2837) and apparently is the first product of nitration of dibromodiphenyl. When nitrated, it was converted into the dinitro-compound, m. p. 148°, which there-

fore has one nitro-group in position 2. It was then found that one bromine atom in the dinitro-compound possessed much greater reactivity than the other.

Hot, concentrated potassium hydroxide had no action on the dinitro-compound, which, however, reacted vigorously with piperidine to give a bromopiperidinodinitrodiphenyl. 4 : 4′-Dibromo-2-nitrodiphenyl and 4 : 4′-dibromo-2 : 2′-dinitrodiphenyl were not affected by piperidine, and it is therefore clear that the above piperidino-derivative is 4-*bromo*-4′-*piperidino*-2 : 3′-*dinitrodiphenyl*, and that the original dinitro-compound is the 2 : 3′-derivative.*

In the entrance of a nitro-group into the B nucleus of dibromodiphenyl (I), the bromophenyl group A apparently has greater directive influence than the bromine atom in B, the nitro-group

(I.)



(II.)

entering position 2, whilst in the nitration of the mononitro-compound (II), conditions are favourable, according to the ordinary theories of substitution, for 3′-nitration in A.

It has similarly been found that the dinitro-derivative of 4 : 4′-dichlorodiphenyl described by Schmidt and Schultz (*Annalen*, 1881, **207**, 340) is 4 : 4′-dichloro-2 : 3′-dinitrodiphenyl. It reacts with piperidine even more readily than does the corresponding dibromo-compound, giving 4-*chloro*-4′-*piperidino*-2 : 3′-*dinitrodiphenyl*. The relative activation, by a nitro-group, of a chlorine and a bromine atom is a subject it is hoped to investigate later on.

The diamine referred to above is therefore 4 : 4′-*dibromo*-2 : 3′-*diaminodiphenyl*. Schultz (*loc. cit.*), by oxidising this substance, obtained what he called a bromaminobenzoic acid, m. p. 155°. This was probably a mixture of 4-bromo-2-amino- and 4-bromo-3-amino-benzoic acids, which melt respectively at 225° and 222°. Further, Strasser and Schultz (*Annalen*, 1881, **210**, 194), by reducing, and thus debrominating, the diamine, obtained a base which they called γ-benzidine. This is evidently 2 : 3′-diaminodiphenyl.

A preliminary investigation has shown that the nitration of 4 : 4′-ditolyl affords, first, a mononitro-compound, m. p. 91—92°,

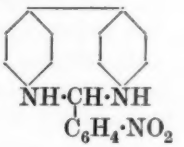
* It might be objected that in the nitration of dibromodiphenyl, both nitro-groups could enter the same nucleus. Against this objection, however, are at least three facts: (1) the difficulty of introducing a third substituent into one nucleus of diphenyl compounds other than hydroxy- and amino-derivatives, (2) the reactivity of one bromine atom in the dinitro-compound, which, if nitration occurred twice in the same nucleus, would almost certainly be 4 : 4′-dibromo-2 : 6-dinitrodiphenyl, *i.e.*, a compound containing no reactive bromine atom, and (3) the quantitative nature of the nitration.

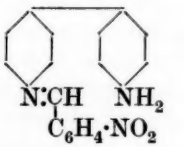
and then a dinitro-compound, m. p. 119°. The latter we regard as the 2 : 3′-dinitro-compound. Ullmann and Frentzel (*Ber.*, 1905, **38**, 726) have described the 3 : 3′(3 : 5′ ?)-derivative, which for present purposes has been prepared by heating 4-iodo-2-nitrotoluene with copper bronze.

The preparation of compounds containing amino-groups in the 3 : 3′- or 3 : 5′-positions in the diphenyl molecule is a matter of considerable difficulty. According to Ullmann and Frentzel (*loc. cit.*), when *m*-nitrobenzenediazonium sulphate is added, under certain conditions, to cuprous chloride and hydrochloric acid, the chief product is 3 : 3′(3 : 5′ ?)-dinitrodiphenyl. We have found, on the contrary, that excellent yields of *m*-chloronitrobenzene are invariably obtained (compare Emde, *Apoth. Ztg.*, 1915, **30**, 293). The dinitro-compound may be obtained from *m*-iodonitrobenzene as stated by Ullmann and Bielecki (*loc. cit.*). The latter substance is only obtainable in small yields by the method of Jacobson, Fertsch, and Heubach (*Annalen*, 1898, **303**, 338), but this difficulty has now been overcome.

During some experiments on the condensation of aldehydes with benzidine, we prepared from *p*-nitrobenzaldehyde a compound to which Barzilowski (*J. Russ. Phys. Chem. Soc.*, 1891, **23**, 69) had assigned formula (III). We have found that this compound readily condenses with a second molecule of a keto-compound, and is therefore (IV).

(III.)





(IV.)

Experimental.

Nitration of 4 : 4′-*Dibromodiphenyl.*—Nitration in glacial acetic acid by Lellmann's method (*loc. cit.*) gave a mononitro-compound, m. p. 124°. Nitration using excess of nitric acid (*d* 1·5) gave a crude dinitro-compound, m. p. 130—135°, which, after being once crystallised from benzene, melted at 148°. A small quantity of the mononitro-compound was obtained from the mother-liquors.

The dinitro-compound was not affected when boiled with very concentrated aqueous potassium hydroxide, whilst alcoholic alkali led to a black product which will be investigated in due course.

Preparation of 4 : 4′-*Dibromo*-2-*nitrodiphenyl.*—2-Nitrobenzidine sulphate was ground into a fine paste with a little water and diazotised at 5°. The solution was poured with vigorous shaking into a cold suspension of cuprous bromide in hydrobromic acid–sodium

bromide. The vigorous reaction over, the whole was heated at 100° for a short time and the gummy solid was collected and warmed with sodium hydroxide to remove phenolic substances. The yellow residue, containing considerable quantities of benzerythrene derivatives, after several crystallisations from alcohol and benzene, melted at 124°. The m. p. was not affected by admixture with the first-named nitro-compound (Found: Br, 4·5. $C_{12}H_7O_2NBr_2$ requires Br, 4·5%).

Nitration of 4 : 4′-*Dibromo*-2-*nitrodiphenyl*.—This substance was dissolved in two parts of warm nitric acid (*d* 1·5). On cooling, pale yellow needles separated, which, after crystallisation from benzene, melted at 148° and did not depress the m. p. of the above dinitro-compound having the same m. p.

4-*Bromo*-4′-*piperidino*-2 : 3′-*dinitrodiphenyl*.—The dinitro-compound, m. p. 148°, was gently warmed with a little piperidine for about a minute. An orange colour at once developed, and, on cooling, the whole set to a crystalline paste owing to the separation of piperidine hydrobromide. It was treated with water, and the orange-red solid so obtained once crystallised from alcohol; the *piperidino*-compound was then obtained in orange-red needles, m. p. 136—137° (Found: Br, 19·3. $C_{17}H_{16}O_4N_3Br$ requires Br, 19·7%). The piperidino-compound was unaffected by further heating with piperidine.

4 : 4′-Dibromo-2-nitro- and 4 : 4′-dibromo-2 : 2′-dinitro-diphenyl were also heated for several minutes with piperidine. In both cases the compounds were recovered unchanged.

Preparation of 4 : 4′-*Dibromo*-2 : 3′-*diaminodiphenyl*.—The corresponding dinitro-compound was reduced with iron, water, and ferric chloride (Roberts and Turner, J., 1925, **127**, 2004). The properties of the diamine agreed with those recorded in the literature. It condensed with salicylaldehyde, but not with carbon disulphide, under conditions similar to those under which benzidine readily condenses with this substance.

Disalicylidene-4 : 4′-*dibromo*-2 : 3′-*diaminodiphenyl* separates from benzene as a yellow, crystalline powder, m. p. 195° (Found: N, 5·1. $C_{26}H_{18}O_2N_2Br_2$ requires N, 5·1%).

Nitration of 4 : 4′-*Dichlorodiphenyl*.—The dichloro-compound readily dissolved in warm nitric acid (*d* 1·5), and, on cooling, the dinitro-compound crystallised out. After washing and drying, it was once crystallised from alcohol and then had m. p. 140°.

4-*Chloro*-4′-*piperidino*-2 : 3′-*dinitrodiphenyl*.—The dichloro-compound was warmed for a few seconds with piperidine, the mixture diluted, and the product filtered off, washed with water, and crystallised from alcohol; the *piperidino*-compound was then obtained in

orange needles, m. p. 132° (Found: Cl, 10·0. $C_{17}H_{16}O_4N_3Cl$ requires Cl, 9·8%). The piperidino-compound was not affected by further heating with piperidine, which also had no effect on 4 : 4′-dichloro-2 : 2′-dinitrodiphenyl prepared from 2 : 5-dichloronitrobenzene by the method of Ullmann and Bielecki (*loc. cit.*).

*Preparation of Mononitro-*4 : 4′*-ditolyl.*—A solution of ditolyl in glacial acetic acid containing one equivalent of nitric acid (*d* 1·4) was evaporated until, on cooling, yellow prisms separated. These, after crystallisation from alcohol, melted at 91—92° (Found: N, 6·2. $C_{14}H_{13}O_2N$ requires N, 6·1%). The nitro-compound is readily soluble in alcohol, acetic acid, or benzene. Ditolyl is unaffected when dissolved in cold acetic–nitric acid mixtures.

*Preparation of Dinitro-*4 : 4′*-ditolyl.*—Sufficient nitric acid (*d* 1·5) was added to the hydrocarbon to form a clear solution, without cooling. On leaving, slender, yellow needles separated. These, after being collected, washed with water, and crystallised from alcohol, and then from glacial acetic acid, melted at 119° (Found: N, 10·6. $C_{14}H_{12}O_4N_2$ requires N, 10·3%).

Preparation of 3 : 3′ (3 : 5′ ?)*-Dinitro-*4 : 4′*-ditolyl.*—4-Iodo-2-nitrotoluene was prepared from 2-nitro-*p*-toluidine as follows: the base (30 g.) was diazotised in dilute sulphuric acid, and the product added to a cold and well-shaken solution of 45 g. of potassium iodide in 1 l. of saturated sodium acetate solution. The brown tar which separated rapidly solidified, and was crystallised from alcohol in presence of charcoal. The yield of pure 4-iodo-2-nitrotoluene was 85% of the theoretical quantity. The iodo-compound reacted normally with copper bronze, After 20 minutes' heating at 240°, the whole was heated at 260° for a few minutes, and the cooled product extracted with benzene in presence of charcoal. The benzene was evaporated, and the residue crystallised from alcohol. The dinitroditolyl thus obtained melted at 175—176° and its properties agreed with those described by Ullmann and Frentzel (*loc. cit.*).

Preparation of 3 : 5′*-Dinitrodiphenyl.*—(a) *By the method of Ullmann and Frentzel* (*loc. cit.*). The exact instructions of these authors were carried out on some dozen occasions. In one or two cases, small quantities of impure dinitrodiphenyl were isolated, but in most of the experiments *m*-chloronitrobenzene was obtained in about 85% of the theoretical yield. (*b*) *From* m-*iodonitrobenzene.* The iodo-compound was prepared by the following modification of the usual method (Jacobson, Fertsch, and Heubach, *loc. cit.*). *m*-Nitroaniline (60 g.) was ground with 56 c.c. of concentrated sulphuric acid, 200 c.c. of water were added, and the whole was well ground. The suspension was diazotised at 5° with 30·6 g. of sodium nitrite in 150 c.c. of water; addition of the nitrite solution in three

portions, below the surface of the suspension, diminished the formation of the diazoamino-compound. The filtered diazo-solution was poured in small quantities into a well-shaken, boiling solution of 110 g. of potassium iodide and 230 g. of hydrated sodium acetate in 1·5 l. of water. The mixture was then cooled, extracted with carbon tetrachloride, the extract washed with sodium thiosulphate, dried, evaporated, and the residue distilled under diminished pressure. The yield of *m*-iodonitrobenzene (m. p. 38°, b. p. 145—155°/15 mm.) was 70% of the theoretical. When the iodo-compound was heated with copper bronze as described by Ullmann and Bielecki (*loc. cit.*), an average conversion into dinitrodiphenyl of 40% of the theoretical was obtained.

Reduction of 3 : 5′-*Dinitrodiphenyl.*—The method previously employed by Emde (*loc. cit.*) was found to be unsatisfactory; reduction with iron, water, and ferric chloride also led to small yields of diamine. This readily forms the *disalicylidene* derivative, which separates from benzene in canary-yellow leaflets, m. p. 176—177° (Found: N, 7·3. $C_{26}H_{20}O_2N_2$ requires N, 7·1%).

p-*Nitrobenzylidenesalicylidenebenzidine.*—The product (m. p. 221—222°, Barzilowski, *loc. cit.*) of interaction of *p*-nitrobenzaldehyde (1 mol.) and benzidine (1 mol.) in hot alcoholic solution was heated under reflux with an alcoholic solution of salicylaldehyde (excess). The red colour of the suspended solid rapidly changed to yellow, and after 30 minutes' boiling the precipitate was collected and crystallised from benzene; yellow prisms, m. p. 210°, were then obtained (Found: N, 10·1. $C_{26}H_{19}O_3N_3$ requires N, 10·0%).

p-*Nitrobenzylideneacetylisopropylidenebenzidine.*—*p*-Nitrobenzylidenebenzidine was warmed with acetylacetone, and the solution obtained was diluted with alcohol and allowed to cool; brownish-yellow, warty prisms, m. p. 185°, then separated (Found: N, 10·6. $C_{23}H_{21}O_3N_3$ requires N, 10·9%).

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University of London. [*Received, December 30th,* 1925.]

LXII.—*The Complex Salts of ββ′β″-Triaminotriethylamine with Nickel and Palladium.*

By Frederick George Mann and William Jackson Pope.

We have already shown (*Proc. Roy. Soc.*, 1925, **A**, **109**, 444) that ββ′β″-triaminotriethylamine may act as a tetra-acidic or a triacidic base, according as the tertiary nitrogen atom exerts or does not exert its basicity. The compound thus gives a tri- and a tetra-hydrochloride, and also two platinichlorides,

$$2N(CH_2{\cdot}CH_2{\cdot}NH_2)_3,6HCl,3PtCl_4,10H_2O \quad (I)$$

and $2N(CH_2{\cdot}CH_2{\cdot}NH_2)_3,8HCl,4PtCl_4,20H_2O$ (II), two aurichlorides and two rhodiochlorides. When, however, the base co-ordinates with metals, it acts solely as a tetramine, and two new types of complex salts were described: thus bivalent platinum of co-ordination number 4 furnishes triaminotriethylamineplatinous iodide, [Pt tren]I_2 (III), whilst quadrivalent platinum of co-ordination number 6 gives dichlorotriaminotriethylamineplatinic chloride, [Pt tren Cl_2]Cl_2 (IV). In these formulæ, the symbol "tren" denotes one molecule of the base.

The complex compounds which the base furnishes with nickel have now been prepared, and fall into two distinct classes. It is known that bivalent nickel may show a co-ordination number of 4 or 6, furnishing, for example, tetramminonickel sulphate (V) and hexamminonickel iodide (VI).

(V.) $[Ni(NH_3)_4]SO_4$ (VI.) $[Ni(NH_3)_6]I_2$

(VII.) [Ni tren]SO_4 (VIII.) $[Ni_2tren_3]I_4$

Triaminotriethylamine similarly gives triaminotriethylaminenickelous sulphate (VII) and tristriaminotriethylaminebisnickelous tetraiodide (VIII): these two compounds are of the same general type as (V) and (VI) in that the metal shows a co-ordination number of 4 and 6 respectively, although in the latter class three molecules of the tetramine distributed between two atoms of nickel are required if the metal is to show a co-ordination number of 6.

Each of these two classes of complex nickel compounds possesses distinct points of interest. We have pointed out (*loc. cit.*, p. 446) that in compounds of the type of triaminotriethylamineplatinous iodide (III), it might be expected that less strain on the amine molecule would result if two molecules of the base shared two atoms of the metal, thus giving a compound of the type $[Pt_2tren_2]I_4$. The same applies to triaminotriethylaminenickelous sulphate (VII), a compound which by virtue of its high solubility in water lends itself to further investigation. Molecular weight determinations

show, however, that the sulphate has the normal composition denoted by formula (VII), and that one molecule of the base can actually satisfy one atom of the metal; conductivity measurements point to the same conclusion.

With regard to the compound of co-ordination number 6, tris-triaminotriethylaminebisnickelous tetraiodide (VIII), it is difficult to see how this complex, composed of three molecules of the base arranged around the two nickel octahedra, can be other than dissymmetric; all attempts to resolve the tetraiodide, however, proved fruitless, possibly owing to the rapid racemisation of the active complex.

The base has also been co-ordinated with bivalent palladium to give triaminotriethylaminepalladious iodide, a compound precisely similar to the platinous iodide (III).

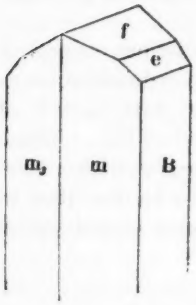
Triaminotriethylamine thus furnishes three distinct types of complex compound, one with bivalent metals of co-ordination number 4, *e.g.*, compounds (III) and (VII), and two with metals of co-ordination number 6, *e.g.*, compounds (IV) and (VIII). These are the first complex compounds to have been prepared with a tetramine; they are, moreover, the first compounds to be described in which an aliphatic tertiary nitrogen atom occupies a co-ordination position.

EXPERIMENTAL.

Preparation of Triaminotriethylaminenickelous Thiocyanate and Tristriaminotriethylaminebisnickelous Tetraiodide.—Nickel succinimide, $[Ni(N{:}C_2O_2{:}C_2H_4)_2 2H_2O],6H_2O$ (Tschugaev, *Ber.*, 1906, **39**, 3197) forms an excellent starting point for the preparation of the co-ordinated derivatives of the metal, since the succinimide residues are easily replaced by aliphatic amines. A mixture of triaminotriethylamine trihydrochloride (32·5 g.) and 33% aqueous caustic soda solution (40·0 c.c.) is therefore warmed on the water-bath until sodium chloride alone remains undissolved. The mixture is poured into a hot solution of nickel succinimide (25·0 g.) in alcohol (750 c.c.). The green solution changes rapidly to blue and is boiled gently for 30 minutes. It is cooled, the precipitated sodium chloride filtered off, and the solution then evaporated gently on the water-bath with the occasional addition of water until it is free from alcohol and of about 60 c.c. in volume. The solution, now of a deep blue, contains a mixture of the two complex ions [Ni tren]$^{\cdot\cdot}$ and $[Ni_2tren_3]^{\cdot\cdot\cdot\cdot}$; these can be isolated readily as the thiocyanate and tetraiodide, respectively. If the solution is poured into a warm strong solution of potassium thiocyanate, the thiocyanate separates as a pale blue powder or deep blue crystals according to the concentration of the nickel solution; if the original solution is poured into hot strong

potassium iodide, the tetraiodide separates as a reddish-violet powder or deep violet crystals. These two compounds and their derivatives will be described in turn.

Triaminotriethylaminenickelous thiocyanate, [Ni tren](SCN)$_2$. The thiocyanate crystallises with great facility from hot aqueous solution in long, very beautiful, deep blue prisms, and two such recrystallisations of the crude product obtained by precipitation with potassium thiocyanate furnish the pure thiocyanate. The latter darkens in colour at 260° and melts with decomposition at 285°; it is soluble in hot, but almost insoluble in cold water [Found: C, 30·1; H, 5·6; N, 26·3; ionised (SCN), 35·95. $C_8H_{18}N_6S_2Ni$ requires C, 29·9; H, 5·65; N, 26·2; 2(SCN), 36·2%]. Very rarely the thiocyanate crystallises in long, narrow, and very thin plates: this form is of the same colour as the prismatic variety, and differs from it apparently only in crystalline habit.



Mr. J. W. Notman of Clare College, working under the direction of Mr. A. Hutchinson, F.R.S., has furnished the following report:

"Triaminotriethylaminenickelous thiocyanate. System, orthorhombic. Class, bipyramidal. $a : b : c = 0{\cdot}736 : 1 : 1{\cdot}167$. The substance occurs in fairly well-developed crystals, of elongated prismatic habit, of which four were measured. Forms present: *B* {010} *m* {110}, *l* {120} observed on one crystal only, *e* {011}, *f* {012}.

				Meas.	Calc.
Angles	mm_3	$110 : 1\bar{1}0$	=	72° 42′	—
	Bm	010 : 110	=	53 33	53° 39′
	Bc	010 : 011	=	40 35	—
	ef	011 : 012	=	19 9	19 9
	ff′	$012 : 0\bar{1}2$	=	60 52	60 32

The crystals were deep blue in colour and, being very opaque, did not lend themselves to optical examination. Some exceedingly thin plates obtained in the case of one preparation enabled straight extinction to be determined."

Both the nickel complexes recorded in this paper are very sensitive to acids, and the addition of hydrochloric acid immediately converts the deep blue of the complex into the pale green of the normal nickel salt. If a warm solution of the thiocyanate is treated with chloroplatinic acid solution, the normal platinichloride (II) of the base is therefore precipitated: if, however, a solution of sodium platinichloride is used, *triaminotriethylaminenickelous platinic tetrachloride dithiocyanate*, [Ni tren]$PtCl_4(SCN)_2$, is precipitated as a russet-brown powder, insoluble in water: it shrinks at 211—213°,

but does not melt below 280° (Found: C, 14·9; H, 2·8; N, 12·8. $C_8H_{18}N_6Cl_4S_2NiPt$ requires C, 14·6; H, 2·8; N, 12·8%).

Triaminotriethylaminenickelous Sulphate, [Ni tren]SO_4,7H_2O.—Hot aqueous solutions of the thiocyanate (6·0 g.) and silver sulphate (5·82 g.) were mixed, and the product, after gently boiling for 15 minutes, was filtered and evaporated down to small bulk on the water-bath. The concentrated solution on cooling deposited deep blue crystals; these were recrystallised from a little hot water, filtered, and dried in air. This sulphate, like normal nickel sulphate, gives a series of hydrates. The product obtained as above is the *heptahydrate* (Found: SO_4, 22·7; H_2O, 29·4. $C_6H_{32}O_{11}N_4SNi$ requires SO_4, 22·5; 7H_2O, 29·5%). The heptahydrate when placed over calcium chloride for 24 hours gives the *dihydrate* as a fine reddish-blue powder (Found: C, 21·3; H, 6·6; SO_4, 28·4. $C_6H_{22}O_6N_4SNi$ requires C, 21·4; H, 6·55; SO_4, 28·5%). The dihydrate on prolonged exposure to calcium chloride, or when heated in a vacuum at 100°, gives the *anhydrous sulphate* as a pale-blue powder, which does not melt below 300° (Found: SO_4, 32·25. $C_6H_{18}O_4N_4SNi$ requires SO_4, 31·9%).

If the anhydrous sulphate has the formula [Ni tren]SO_4, the molecular weight is 300·9, and the "apparent" molecular weight in dilute aqueous solution (if ionisation is complete) is 150·4. If, however, it has the formula [Ni_2tren_2]$(SO_4)_2$, the molecular weight is 601·8, and the "apparent" molecular weight 200·6. The results actually obtained by the cryoscopic method are as follows, *c* being the concentration of the anhydrous sulphate expressed as g. in 100 g. of water:

c	0·422	1·32	1·79	3·23
"Apparent" mol. wt.	160 (157*)	173	180	218

* Calculated value, correct to only two significant figures.

These results furnish strong evidence that the sulphate has the simple formula [Ni tren]SO_4, and that the "apparent" molecular weight approaches to 150 at great dilution, and increases with increasing concentration as the degree of ionisation falls. If the compound possessed the double formula, it could not show an apparent molecular weight of less than 200. This conclusion is confirmed by the close correspondence between the equivalent conductivities of normal nickelous sulphate and triaminotriethylaminenickelous sulphate at 25°.

Vol. (litres) containing 1 g. equiv. of sulphate		128	256	512	1024
Equiv. cond.	$NiSO_4$	88·2	98·9	109·3	117·4
	[Ni tren]SO_4	85·9	96·7	106·0	119·2

The values for nickel sulphate are those given by Franke (*Z. physikal. Chem.*, 1895, **16**, 472), those for the tetramine derivative have been determined by Mr. A. F. H. Ward of Jesus College and Mr. L. F. S. Ward of Trinity College, to whom the authors' thanks are due.

Tristriaminotriethylaminebisnickelous Tetraiodide, $[Ni_2tren_3]I_4,3\frac{1}{2}H_2O$.—The crude reddish-violet iodide obtained by precipitation with potassium iodide in the original preparation is recrystallised three times from hot water, and so obtained in heavy, deep violet crystals: if the hot aqueous solution is too concentrated or is chilled too rapidly, the tetraiodide separates as an oil which subsequently solidifies (Found: C, 18·9; H, 5·4; I, 45·1, 45·1, 45·2; Ni, 10·4, 10·3; H_2O, 5·5. $C_{36}H_{122}O_7N_{24}I_8Ni_4$ requires C, 19·2; H, 5·5; I, 45·1; Ni, 10·4; H_2O, 5·6%). On one occasion when a small quantity of the iodide was rapidly recrystallised from a little hot water, the *dihydrate* separated (Found: C,* 19·5, 19·6; H, 5·2, 5·2; N, 15·15; I, 46·2, 46·0. $C_{18}H_{58}O_2N_{12}I_4Ni_2$ requires C, 19·6; H, 5·3; N, 15·3; I, 46·2%). The anhydrous tetraiodide, obtained by heating either of the above hydrates in a vacuum at 110°, is a pale violet powder, m. p. 307—309° (decomp.) (Found: I, 47·4. $C_{18}H_{54}N_{12}I_4Ni_2$ requires I, 47·6%).

If, after the crude tetraiodide has been precipitated in the original preparation, the filtrate is treated with saturated potassium thiocyanate solution, triaminotriethylaminenickelous thiocyanate separates in fair yield and after two recrystallisations is pure; both complexes can thus be isolated from the same preparation.

The *tetrabromide*, $[Ni_2tren_3]Br_4$, can be obtained in small yield by treating the final solution in the original preparation with strong sodium bromide solution, or in better yield by treating a saturated solution of the tetracamphorsulphonate described later with sodium bromide. It is obtained on recrystallisation as a pale reddish-blue, anhydrous powder, which does not melt below 290° (Found: H, 6·1; Br, 36·4, 36·7; Ni, 13·6. $C_{18}H_{54}N_{12}Br_4Ni_2$ requires H, 6·2; Br, 36·5; Ni, 13·4%).

Attempted Resolution of the Tristriaminotriethylaminebisnickelous Complex, $[Ni_2tren_3]^{\cdots\cdot}$.—The *tetra*-d-α-*bromocamphor*-π-*sulphonate*, $[Ni_2tren_3](C_{10}H_{14}O_4BrS)_4$. Solutions of 16·0 g. of the tetraiodide ($3\frac{1}{2}H_2O$) and 23·56 g. of silver *d*-α-bromocamphor-π-sulphonate, each in 75 c.c. of hot water, were mixed and the product, after gentle

* Throughout this paper, repeated analytical results refer to analyses of different preparations of the compound, and not merely to repeated analyses of the same preparation: the figures given for this dihydrate are the only exception.

boiling, was filtered and evaporated until crystals appeared on the surface. The solution was now cooled and filtered, and the crystalline residue three times recrystallised from water. The anhydrous *tetra*-d-*bromocamphorsulphonate* was thus obtained as a pale violet, crystalline powder, which shrinks at 180° and melts with decomposition at 183—185° (Found: H,* 6·2; Br, 17·8; S, 7·05; Ni, 6·5. $C_{58}H_{110}O_{16}N_{12}Br_4S_4Ni_2$ requires H, 6·2; Br, 17·8; S, 7·1; Ni, 6·5%).

The tetrabromocamphorsulphonate is so slightly soluble in water that it could not be reconverted by double decomposition into the bromide or iodide. The hot aqueous solution was therefore added carefully to a hot dilute solution of sodium picrate, and the *tetrapicrate*, $[Ni_2tren_3](C_6H_2O_7N_3)_4,3H_2O$, precipitated as a fine, dark yellow powder, which when filtered, washed with water and alcohol, and air-dried melted with decomposition at 205—206° (Found: C, 33·25; H, 4·5; N, 22·2. $C_{42}H_{68}O_{31}N_{24}Ni_2$ requires C, 33·1; H, 4·5; N, 22·1%).

This tetrapicrate was found to be identical in composition and melting point with that obtained directly from the tetraiodide; it is only very slightly soluble in boiling water and insoluble in all ordinary organic solvents except formamide. No rotation could be detected in a 0·5% solution of the picrate in formamide in a 2-dcm. tube: stronger solutions could not be used owing to the high absorption of light.

The *tetra*-d-*camphor*-β-*sulphonate*, $[Ni_2tren_3](C_{10}H_{15}O_4S)_4$. Solutions of the tetraiodide (19·0 g.) and silver *d*-camphor-β-sulphonate (22·8 g.), each in warm water (80 c.c.), were mixed, and the product after gentle boiling was filtered and then evaporated until crystals appeared in the solution. The latter was cooled and filtered, and the crystallised product three times recrystallised from warm water. The *tetra*-d-*camphorsulphonate* was thus obtained as a reddish-violet, crystalline powder, which shrinks at 230° and melts at 233—235°: it is appreciably more soluble in water than the corresponding bromocamphorsulphonate (Found: H, 7·8; S, 8·9; Ni, 7·95. $C_{58}H_{114}O_{16}N_{12}S_4Ni_2$ requires H, 7·8; S, 8·7; Ni, 7·9%). A warm solution of the camphorsulphonate was mixed with that of potassium iodide, and the crystals which separated on cooling were rapidly recrystallised from a little hot water, the pure tetraiodide being thus obtained (Found: I, 45·1%). A 2% aqueous solution of this tetraiodide in a 4-dcm. tube gave no perceptible rotation.

Attempts to prepare a crystalline tartrate of the complex failed, only syrupy solutions being obtained.

* All the camphor derivatives (and certain others) recorded in this paper gave low and irregular values for carbon, but satisfactory values for hydrogen.

Triaminotriethylaminenickelous d-*bromocamphorsulphonate*, [Ni tren]$(C_{10}H_{14}O_4BrS)_2,2H_2O$.

Attempts were also made to prepare the above tetra-*d*-bromocamphor-π-sulphonate by double decomposition of the tetraiodide with ammonium *d*-bromocamphorsulphonate. It was found, however, that when solutions of the tetraiodide (4 g.) and an excess of the ammonium sulphonate (6 g.), each in warm water (20 c.c.), were mixed, and the product warmed on the water-bath, ammonia was evolved, and crystals soon appeared on the surface. This product was twice recrystallised from warm water, and finally obtained as beautiful, bluish-violet, crystalline plates. These on analysis proved to be *triaminotriethylaminenickelous* d-*bromocamphorsulphonate* (Found: Br, 18·6; S, 7·5; Ni, 6·65; H_2O, 4·2. $C_{26}H_{50}O_{10}N_4Br_2S_2Ni$ requires Br, 18·55; S, 7·4; Ni, 6·8; $2H_2O$, 4·2%). Heating in a vacuum at 110° gives the pale blue, anhydrous product, m. p. 263—266° (decomp.). The identity of this compound was further confirmed by treating its warm aqueous solution with potassium thiocyanate solution, when triaminotriethylaminenickelous thiocyanate separated, and when once recrystallised was pure (Found: N, 25·85%). This degradation of the nickel complex of co-ordination number 6 to that of co-ordination number 4 by the action of an ammonium salt was found to be general, and to follow presumably the equation $[Ni_2tren_3]X_4 + 4NH_4X' = 2[Ni\ \ tren]X_2 + tren\ 4HX' + 4NH_3$. It is noteworthy that the third molecule of the tetramine in the higher complex is evicted but not replaced by the ammonia under these conditions, and all attempts made to prepare compounds having the complex [Ni tren$(NH_3)_2$]$^{\cdot\cdot}$ failed. In the particular case of the *d*-bromocamphorsulphonate described above, the colours of the dihydrate (bluish-violet) and the anhydrous product (pale blue) are characteristic of nickel complexes having co-ordination numbers of 6 and 4 respectively, and therefore the dihydrate has probably the composition

[Ni tren$(H_2O)_2$]$(C_{10}H_{14}O_4BrS)_2$.

Triaminotriethylaminepalladious Iodide, [Pd tren]I_2.—A warm solution of triaminotriethylamine trihydrochloride (5·4 g.) in 33% aqueous caustic soda solution (7·4 c.c.) is added to a solution of palladium dichloride (3·0 g.) in hot water (70 c.c.). An amorphous, yellow precipitate at once appears, but redissolves when the solution is heated on the water-bath. After heating for 2 hours, the solution is evaporated to small bulk, filtered, and mixed with warm strong potassium iodide solution. The cream-coloured precipitate is filtered off, and recrystallised from much hot water, in which the iodide is only moderately soluble. The *triaminotriethylaminepalladious iodide* is thus obtained as a fine, cream-coloured powder,

which after drying over sulphuric acid darkens in colour at 220° and melts at 224—226° (decomp.) (Found : C, 14·1; H, 3·9; I, 49·6; Pd, 20·9. $C_6H_{18}N_4I_2Pd$ requires C, 14·2; H, 3·6; I, 50·1; Pd, 21·1%).

If instead of adding potassium iodide to the above solution, the latter is chilled, made just acid with hydrochloric acid, and treated with an excess of dilute palladium dichloride solution, a fine dark brown precipitate separates. The latter redissolves if the solution is warmed, and on filtering and cooling, long, chocolate-coloured needles separate. These crystals decompose largely if an attempt is made to recrystallise them from boiling water, and their identity is therefore uncertain; they would appear to be *triaminotriethylamine-palladious palladiochloride*, [Pd tren]$PdCl_6,H_2O$, and owe their formation presumably to partial atmospheric oxidation of the palladious chloride solution (Found : C, 12·3; H, 3·8; Cl, 35·3; Pd, 35·7. $C_6H_{20}ON_4Cl_6Pd_2$ requires C, 12·2; H, 3·4; Cl, 36·0; Pd, 36·15%).

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LXIII.—$\gamma\gamma'\gamma''$-*Triaminotripropylamine and its Complex Compounds with Nickel.*

By FREDERICK GEORGE MANN and WILLIAM JACKSON POPE.

THE preparation of $\gamma\gamma'\gamma''$-triaminotripropylamine is similar to that of $\beta\beta'\beta''$-triaminotriethylamine, for molten phthal-γ-bromopropylimide on treatment with gaseous ammonia gives $\gamma\gamma'\gamma''$-triphthalimidotripropylamine hydrobromide, which on hydrolysis furnishes the required base. Whereas, however, the tertiary nitrogen atom in triaminotriethylamine is so feebly basic that the amine may act as a tri- or a tetra-acidic base, that in triaminotripropylamine, by virtue of its greater distance from the primary amine groups, is strongly basic, and the amine therefore always acts as a tetra-acidic base. The strongly basic character of the tertiary amine group in triaminotripropylamine causes the synthesis to follow a rather different course from that of the corresponding ethyl base. Ammonia reacts with phthal-β-bromoethylimide to give triphthalimidotriethylamine, mixed with about 12% of the hydrobromide of this base : phthal-γ-bromopropylimide, however, gives solely triphthalimidotripropylamine hydrobromide, and none of the free base. The hydrobromide, moreover, is largely contaminated with various amorphous by-products, and the yield of the triphthalimido-compound is therefore low.

It has been shown (preceding paper) that nickel succinimide on treatment with triaminotriethylamine gives a mixture of two com-

plex ions, the bivalent triaminotriethylaminenickelous ion, [Ni tren]$^{\cdot\cdot}$, in which the metal shows a co-ordination number of 4, and the quadrivalent tristriaminotriethylaminebisnickelous ion, [Ni_2 $tren_3$]$^{\cdot\cdot\cdot\cdot}$, in which the metal has a co-ordination number of 6. Nickel succinimide on treatment with triaminotripropylamine gives, however, one complex of the first type only, and the triaminotripropylaminenickelous ion, [Ni trpn]$^{\cdot\cdot}$, in which the metal shows a co-ordination number of 4, can be precipitated as the thiocyanate. The symbol "trpn" is here used to denote one molecule of the tetramine. This complex ion is less stable and less strongly electropositive than the corresponding ethyl complex ion; the thiocyanate undergoes slight decomposition even on recrystallisation from hot water, whilst precipitation with potassium iodide in the original preparation furnishes the hydroxy-iodide of the above complex. The normal iodide is prepared by the double decomposition of some far more stable salt such as the nitrate.

No complex compound of triaminotripropylamine with nickel or with platinum in which the metal showed a co-ordination number of 6 could be isolated. It would seem, therefore, that the very well defined dichlorotriaminotriethylamineplatinic chloride,

$$[Cl_2Pt\ tren]Cl_2,$$

has no stable propyl homologue.

EXPERIMENTAL.

Triphthalimidotripropylamine Hydrobromide,

$$\left(C_6H_4\!<\!\begin{matrix}CO\\CO\end{matrix}\!>\!N\cdot CH_2\cdot CH_2\cdot CH_2\right)_3N,HBr.$$

—A stream of dry ammonia gas is passed through molten phthal-γ-bromopropylimide at 150° until the product becomes too viscous to allow further passage of the gas, the reaction being about twice as rapid as that with phthal-β-bromoethylimide under like conditions. The cold pale-yellow product (with containing tube) is pulverised, and twice extracted with boiling alcohol: the residue is washed with water, and then recrystallised from hot acetic acid. The solution, when filtered and cooled, deposits *$\gamma\gamma'\gamma''$-triphthalimidotripropylamine hydrobromide* with one molecule of acetic acid of crystallisation. This product, when washed with acetic acid and ether and dried in the air, is pure; on heating, it liberates acetic acid at 100—105°, and finally melts at 243—244°, *i.e.*, at the melting point of the hydrobromide itself (Found: C, 58·5; H, 5·0; Br, 11·4. $C_{35}H_{35}O_8N_4Br$ requires C, 58·4; H, 4·9; Br, 11·1%). The *hydrobromide* itself can be obtained by heating the above product in a vacuum at 100°, or by crystallisation from a large volume of very dilute hydrobromic acid, from which the

hydrobromide separates in colourless needles, m. p. 243—245° (Found: Br, 12·1. $C_{33}H_{31}O_6N_4Br$ requires Br, 12·1%).

Triphthalimidotripropylamine, $(C_6H_4{:}C_2O_2{:}N{\cdot}C_3H_6)_3N$.—The hydrobromide with acetic acid of crystallisation (2 g.) is dissolved in boiling water (450 c.c.), and to the clear solution is added a slight excess of *N*-sodium hydroxide (6·0 c.c.). A white precipitate of *triphthalimidotripropylamine* immediately separates, and when filtered, washed with boiling water, and twice recrystallised from alcohol, is obtained in fine needles, m. p. 150—151° (Found: C, 68·8; H, 5·2. $C_{33}H_{30}O_6N_4$ requires C, 68·5; H, 5·2%).

γγ′γ″-Triaminotripropylamine Tetrahydrochloride,

$$N(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)_3,4HCl,\tfrac{1}{2}H_2O.$$

—Triphthalimidotripropylamine hydrobromide with acetic acid of crystallisation (10 g.) and hydrochloric acid (300 c.c., 1 : 1 by volume) are boiled under reflux. The solution becomes clear in about 4 hours, and after 7 hours is chilled, the phthalic acid separated, and the filtrate evaporated to small bulk. The tetrahydrochloride is so soluble in water that it cannot be crystallised, and prolonged evaporation of its solution merely gives a syrup: the concentrated solution is therefore poured into alcohol, and the heavy syrup which separates, solidifies on standing and stirring to a crystalline mass of the tetrahydrochloride, which is filtered off and washed with alcohol. The *tetrahydrochloride* is thus obtained as slightly deliquescent, white crystals which melt with foaming at 227—229°; the water of crystallisation is not liberated on heating in a vacuum at 100° (Found: C, 31·1; H, 8·2; Cl, 41·3, 41·7. $C_{18}H_{58}ON_8Cl_8$ requires C, 31·5; H, 8·45; Cl, 41·3%).

Triaminotripropylamine platinichloride,

$$N(C_3H_6{\cdot}NH_2)_3,4HCl,2PtCl_4,3H_2O,$$

is prepared in the usual way, and when recrystallised from a little water separates in orange-coloured needles (Found: C, 10·3; H, 3·2; Pt, 36·7; H_2O, 4·9. $C_9H_{34}O_3N_4Cl_{12}Pt_2$ requires C, 10·2; H, 3·2; Pt, 36·8; $3H_2O$, 5·1%). The anhydrous material darkens at 250° and melts with decomposition at 257—258°.

Triaminotripropylamine aurichloride,

$$N(C_3H_6{\cdot}NH_2)_3,4HCl,4AuCl_3,3H_2O,$$

separates when concentrated solutions of the tetrahydrochloride and of potassium aurichloride are mixed. It is filtered, washed with water, and dried without recrystallisation; the orange-yellow needles, m. p. 191—192° (decomp.), are even more soluble in alcohol and acetone than in water (Found: C, 6·9; H, 2·0; Au, 49·4, 49·5. $C_9H_{34}O_3N_4Cl_{16}Au_4$ requires C, 6·75; H, 2·1; Au, 49·2%).

Triaminotripropylamine picrate, $N(C_3H_6{\cdot}NH_2)_3,4C_6H_4O_7N_3,H_2O$, is almost insoluble in the usual liquids, but can be recrystallised

from boiling water, one litre of which dissolves about 1 g. of the picrate. The latter separates in pale yellow needles which soften at 190° and melt with decomposition at 222° (Found: C, 35·2; H, 3·5. $C_{33}H_{38}O_{29}N_{16}$ requires C, 35·3; H, 3·4%).

Tribenzoyltriaminotripropylamine, $N(C_3H_6{\cdot}NH{\cdot}CO{\cdot}C_6H_5)_3$, prepared in the usual way, is obtained after three recrystallisations from anhydrous acetone as fine, white crystals, m. p. 129—131° (Found: C, 72·1; H, 7·2. $C_{30}H_{36}O_3N_4$ requires C, 71·9; H, 7·25%).

The Co-ordination Derivatives of Triaminotripropylamine.

Triaminotripropylaminenickelous thiocyanate, [Ni trpn]$(SCN)_2$.—The tetrahydrochloride of the base (12·0 g.) is warmed with 33% aqueous caustic soda solution (16·0 c.c.) until sodium chloride alone remains undissolved: the mixture is then added to a hot solution of nickel succinimide (8·5 g.) in alcohol (250 c.c.). The colour of the solution changes rapidly from pale green to blue. The solution is now treated precisely as in the preparation of the corresponding ethyl derivative (p. 483), and the concentrated aqueous solution is filtered directly into a cold strong solution of potassium thiocyanate. The fine precipitate is filtered off and twice recrystallised from hot water, from which the *triaminotripropylaminenickelous thiocyanate* separates on rapid cooling in pale lilac-blue, crystalline leaflets, and on slow cooling in long needles of the same colour. The difference between these two forms, as in the case of the corresponding ethyl derivative, is apparently solely one of crystalline habit (Found: C, 36·6; H, 6·55; Ni, 16·2. $C_{11}H_{24}N_6S_2Ni$ requires C, 36·4; H, 6·7; Ni, 16·2%). The thiocyanate melts at 260—261° with decomposition; it is far less stable than the corresponding ethyl compound, and when recrystallised from hot water always leaves behind on the filter a small quantity of an amorphous green product, presumably nickel hydroxide.

Triaminotripropylaminenickelous Iodide, [Ni trpn]I_2,$1\frac{1}{2}H_2O$.—The thiocyanate in hot aqueous solution is treated with a solution of the calculated quantity of silver nitrate, and the product, after filtering, evaporated to small bulk. The cold concentrated solution is added to a cold saturated potassium iodide solution, and the crystalline precipitate filtered off and washed with a little water, alcohol, and ether. The *iodide* is thus obtained as a fine, apple-green, crystalline powder (Found: I, 48·05; Ni, 11·0. $C_{18}H_{54}O_3N_8I_4Ni_2$ requires I, 48·1; Ni, 11·1%).

Triaminotripropylaminenickelous Hydroxyiodide,

[Ni trpn]I(OH),$2H_2O$.

—If the warm concentrated aqueous solution obtained by treating nickel succinimide with the amine is mixed with about twice its

volume of hot strong potassium iodide solution, fine, sea-green, crystalline leaflets rapidly appear. These crystals consist of the above *hydroxyiodide* combined with potassium iodide, and have the composition 2[Ni trpn]I(OH),KI,$2H_2O$. This compound is decomposed, however, even by cold water, and the preparation of the pure material is therefore almost impossible: slight dissociation occurs when the crystals are washed even with a little alcohol to free them from mother-liquor, and various preparations always give in consequence a low iodine and high carbon value (Found: C, 22·7; H, 5·3; N, 11·0; I, 37·7; Ni, 11·5. $C_{18}H_{54}O_4N_8I_3NiK$ requires C, 22·0; H, 5·5; N, 11·4; I, 38·7; Ni, 11·9%).

If the mother-liquor after the separation of these crystals is treated further with potassium thiocyanate solution, a small precipitate of triaminotripropylaminenickelous thiocyanate is obtained.

When the green crystals of the potassium iodide addition product are dissolved in warm water, a deep blue solution is at once obtained, and, on cooling, deep blue crystals of *triaminotripropylaminenickelous hydroxyiodide*, [Ni trpn]I(OH),$2H_2O$, separate. The hydroxyiodide is quite stable in the presence of water, and can be recrystallised repeatedly from boiling water without apparent change (Found: C, 25·5; H, 6·3; N, 13·0; I, 29·5; Ni, 13·5. $C_9H_{29}O_3N_4INi$ requires C, 25·3; H, 6·85; N, 13·1; I, 29·7; Ni, 13·75%). This compound when heated in a vacuum at 100° readily loses its water of crystallisation, but at the same time undergoes slight further hydrolysis, and the anhydrous product is therefore never quite pure. When the hydroxyiodide in strong aqueous solution is treated with strong potassium iodide solution, the sea-green crystals of the above potassium iodide addition product once again separate, and when recrystallised from water again furnish the pure deep blue hydroxyiodide. Moreover, when the hydroxyiodide in aqueous solution is treated with potassium thiocyanate solution, a rapid precipitation of triaminotripropylaminenickelous thiocyanate occurs, and the latter when once recrystallised from hot water is pure (Found: N, 23·2. $C_{11}H_{24}N_6S_2Ni$ requires N, 23·2%). Aqueous solutions of the hydroxyiodide are distinctly alkaline, and on exposure to air absorb carbon dioxide.

In view of the ready formation and great stability of dichlorotriaminotriethylamineplatinic chloride, [Cl_2Pt tren]Cl_2 (p. 482) many experiments were made to prepare the corresponding propyl derivative. No definite evidence of the formation of such a compound could be obtained, however, and the attempt was finally abandoned.

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LXIV.—*The Resolution of* dl-*Alanine and the Formation of* trans-2 : 5-*Dimethylpiperazine.*

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THE α-2 : 5-dimethylpiperazine of Stoehr (*J. pr. Chem.*, 1893, **47**, 494; 1897, **55**, 49) was identified by Pope and Read (J., 1912, **101**, 2327; 1914, **105**, 219) as the *trans*-isomeride; the same compound was obtained by Hoyer (*Z. physiol. Chem.*, 1902, **34**, 347) by the reduction of lactimide, $NH<^{CO\cdot CHMe}_{CHMe\cdot CO}>NH$. The latter compound would therefore appear to be internally compensated or *trans*-3 : 6-diketo-2 : 5-dimethylpiperazine produced by anhydride formation from a molecule each of *d*- and *l*-alanine; this conclusion, as will be shown later, is not necessarily correct. The two optically active alanines, on the other hand, yield optically active anhydrides (E. Fischer, *Ber.*, 1906, **39**, 453) which are necessarily the *d*- and *l-cis*-3 : 6-diketo-2 : 5-dimethylpiperazines. It might be expected that on reduction the latter substances would yield the *d*- and *l-cis*-2 : 5-dimethylpiperazines; the racemic compound of these two isomerides should be represented by the β-2 : 5-dimethylpiperazine of Stoehr (*loc. cit.*), but Pope and Read were unable to separate such a compound from the material which they examined.

It thus seemed desirable to reduce the anhydride of one of the optically active alanine anhydrides or *cis*-3 : 6-diketo-2 : 5-dimethylpiperazines for the purpose of isolating and further characterising the *d*- and *l-cis*-2 : 5-dimethylpiperazines which were presumably associated in Stoehr's β-compound. A certain quantity of *d*-alanine was prepared by the hydrolysis of silk as described by Fischer (*Ber.*, 1906, **39**, 462), but the process, although satisfactory, is tedious. The preparation was hastened by preparing *dl*-alanine from acetaldehyde, potassium cyanide and ammonium chloride by the method of Zelinsky and Stadnikov (*Ber.*, 1908, **41**, 2061) and resolving this into its optically active components.

Fischer (*Ber.*, 1899, **32**, 2459) resolved benzoyl-*dl*-alanine by crystallisation with cinchonine, and Gibson and Pope (J., 1912, **101**, 939) improved this method by the alternate use of strychnine and brucine; the hydrolysis to *d*- and *l*-alanine proceeds, however, only with difficulty. Gibson and Simonsen (J., 1915, **107**, 798) resolved *dl-p*-toluenesulphonylalanine by crystallisation with strychnine and brucine, and Colombano and Sanna (*Atti R. Accad. Lincei*, 1913, **22**, ii, 292) resolved *dl*-alanine by crystallising its ethyl ester with *d*-bromocamphorsulphonic acid.

None of these methods proved satisfactory for preparing the

optically active alanines in quantity and we therefore devised a new one. It was found that *d*-hydroxymethylenecamphor and *d*-chloromethylenecamphor do not condense with *dl*-alanine, but that condensation occurs readily with the ethyl ester of alanine; the method of resolution by means of *d*-hydroxymethylenecamphor described by Pope and Read (J., 1914, **105**, 219) is therefore applicable and the condensation products can be hydrolysed by concentrated hydrochloric acid, yielding the optically active alanines. This method of resolving *dl*-alanine seems to be the most convenient yet described; by its aid *l*-alanine has been separated in quantity from the racemic compound.

Several methods for converting the *d*- and *l*-alanines into the *d*- and *l-cis*-3 : 6-diketo-2 : 5-dimethylpiperazines, or the optically active lactimides, were studied. Hoyer's method of heating alanine in dry hydrogen chloride at 180—200°, boiling the product with lead hydroxide, and removing the metal by hydrogen sulphide gave poor yields. One method described by Fischer (*Ber.*, 1906, **39**, 467), in which the ethyl ester of alanylalanine, prepared from alanine ethyl ester and alanyl chloride, is treated with gaseous ammonia, also gives poor yields. Fischer's second method (*Ber.*, 1906, **39**, 543), in which the ethyl ester of alanine is preserved for several weeks, is satisfactory and gives a yield of about 70%.

When the optically active lactimides, which have necessarily the *cis*-configuration, were reduced with sodium and alcohol, the chief product, and indeed the only one which could be isolated, was the potentially optically inactive *trans*-2 : 5-dimethylpiperazine identified by Pope and Read. It thus seems clear that the lactimide undergoes enolisation during reduction in accordance with the scheme

$$\mathrm{NH}\!<\!\begin{matrix}\mathrm{CO\cdot CHMe}\\ \mathrm{CHMe\cdot CO}\end{matrix}\!>\!\mathrm{NH} \longrightarrow \mathrm{NH}\!<\!\begin{matrix}\mathrm{C(OH){:}CMe}\\ \mathrm{CMe{:}C(OH)}\end{matrix}\!>\!\mathrm{NH}$$

$$\longrightarrow \mathrm{NH}\!<\!\begin{matrix}\mathrm{CH_2\cdot CHMe}\\ \mathrm{CHMe\cdot CH_2}\end{matrix}\!>\!\mathrm{NH},$$

and that the original *cis*-compound thus becomes converted into the *trans*-2 : 5-dimethylpiperazine accompanied by little, if any, of the *cis*-isomeride. No evidence is thus obtainable as to whether inactive lactimide is the racemic or *cis*-compound or the internally compensated or *trans*-compound.

Experimental.

dl-Alanine, prepared by Zelinsky and Stadinov's method, was converted into its ethyl ester, which was then heated for 2 hours on the water-bath with an equimolecular quantity of *d*-hydroxymethylenecamphor. On pouring into water, extracting with light

petroleum, and evaporating the petroleum solution after drying with potassium carbonate, an oil was obtained which readily crystallised; the crystalline product was repeatedly crystallised from light petroleum until its melting point became constant at 108—109°. The substance thus obtained in long, white needles is the d-*methylene-camphor*-l-*alanine ethyl* ester, $C_8H_{14}<\begin{matrix}C{:}CH\cdot NH\cdot CHMe\cdot CO_2Et\\ CO\end{matrix}$

(Found: C, 68·9; H, 8·9. $C_{16}H_{25}O_3N$ requires C, 68·8; H, 9·0%). The substance is so soluble in most organic solvents that it can only be conveniently crystallised from light petroleum. 0·1008 Gram, made up to 20 c.c. with absolute alcohol, gave $\alpha_{\text{Hg green}} = +2{\cdot}58°$ in a 2-dcm. tube at 20°; whence $[\alpha]_{\text{Hg green}} = +256°$.

This compound, when treated by the bromine method of Pope and Read, yielded only resinous products from which alanine could not be separated; it is, however, hydrolysed by distillation in steam after admixture with concentrated hydrochloric acid. Hydroxymethylenecamphor distils away and *l*-alanine hydrochloride remains behind; the hydrochloric acid is removed with the aid of lead hydroxide, the excess of the latter by hydrogen sulphide, and the *l*-alanine then separated by crystallisation from the residual aqueous solution. 1·8761 Gram, made up to 20 c.c. with 1·25*N*-hydrochloric acid solution, gave $\alpha_{\text{Hg green}} = -3{\cdot}22°$ in a 2-dcm. tube at 20°; whence $[\alpha]_{\text{Hg green}} = -12{\cdot}2°$; this value is numerically identical with that given by *d*-alanine prepared from silk, but is, of course, of opposite sign. This simple type of method will be further studied in its applications to the resolution of racemic aminocarboxylic acids.

Reduction of l-*Lactimide.*—*l*-Alanine was converted into its ethyl ester and preserved for several weeks until solidification had apparently become complete; after crystallisation from alcohol a 70% yield of *l*-lactimide was obtained. The product melted at 272° and showed $[\alpha]_D^{20°} = +29{\cdot}1°$ in a 2% alcoholic solution. The *l*-lactimide (6 g.) was treated with absolute alcohol (300 c.c.), and sodium (32 g.) gradually added with constant shaking. After removal of the alcohol, the reduction product was benzoylated; the only separable product was the optically inactive dibenzoyl-*trans*-2 : 5-dimethylpiperazine (0·8 g.) of Pope and Read. The identity of the product was confirmed by mixed melting-point determinations with a sample of the latter substance; each, and the mixtures, melted at 227—228°.

No better yields were obtained by reducing the *l*-lactimide in amyl-alcoholic solution and it is noteworthy that Gaurilov (*Bull. Soc. chim.*, 1925, **37**, 1651) obtained only a 15% yield of piperazine by this mode of reducing 2 : 5-diketopiperazine. The lactimide

could not be reduced by colloidal palladium or platinum, by calcium or calcium hydride and alcohol, or by aluminium amalgam in aqueous-alcoholic solution.

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NOTES.

Air Oxidation of Titanous Sulphate Solution. Vanadous Sulphate, a New and Powerful Reducing Agent. By A. S. RUSSELL.

THE powerful reducing agent, titanous sulphate, is used less than it might be on account of the trouble of preserving it from oxidation by air. I am not aware than any worker with this reagent has said that this is unnecessary. Knecht and Hibbert ("New Reduction Methods in Volumetric Analysis," 2nd ed., 1925, p. 62), who have the largest experience of this reagent, say that any results obtained without taking the precaution of preventing air oxidation are valueless. My experience is different. When a solution of titanous sulphate in 4*N*-sulphuric acid is prepared from titanic sulphate by Nakazono's rapid method (*J. Chem. Soc. Japan*, 1921, **42**, 526), and kept in a burette exposed to air, I find that its titre when standardised with *N*/10-permanganate remains constant for 12 hours. It follows that precautions to exclude air are unnecessary. It is also a consequence that if titanium itself be determined by reducing titanic sulphate with zinc amalgam and titrating the liquid after separation with permanganate, the work can be carried out in air if the acidity of the titanium solution is 4*N*-sulphuric acid. I confirmed this by alternately reducing with zinc amalgam and oxidising with *N*/10-permanganate four times a volume of titanic sulphate of known concentration without excluding air. The titres were constant and equal to that calculated on the assumption that the reduction was quantitative. Titanous sulphate thus resembles ferrous and uranous sulphates in being stable in air at the ordinary temperature if in 4*N*-sulphuric acid.

It is not necessary to adopt the excellent but elaborate method of Knecht and Hibbert (*op. cit.*, p. 63) for preserving titanous sulphate solution for a long time. It is simpler to have a solution of titanic sulphate in 4*N*-sulphuric acid and, whenever titanous sulphate is needed, to reduce the volume required with zinc amalgam for 1 minute, decant the liquid into a flask, transfer to a burette, and

immediately before use standardise it against $N/10$-permanganate. I find it is not oxidised by the air when run into hot or boiling solutions reduced by it. I find also that titanous sulphate is not less powerful as a reducing agent than the chloride and that the reducing power is unaffected by the presence of the free sulphuric acid. The sulphate solution is consequently simpler to use than the chloride, because in practice back titrations are done with permanganate as well as with ferric alum.

Vanadous sulphate has not, I think, been previously used as a reducing agent. I find that it is a more powerful reducing agent than titanous sulphate, reducing with greater ease all the inorganic and organic substances reduced by the latter. It reduces titanic sulphate itself in the cold. It lies between cadmium and tin in its reducing power in $2N$-sulphuric acid, whereas titanous sulphate was found to lie between lead and copper. It is, as is to be expected, much more susceptible to air oxidation, but not to such an extent that precautions to exclude air when using it are essential. A $N/10$-solution in $10N$-sulphuric acid is not measurably oxidised by air when kept for an hour in a burette. It may therefore be used without excluding air in volumetric work which can be completed within that time. It is prepared by the same method and as quickly as titanous sulphate.—DR. LEE'S LABORATORY, CHRIST CHURCH, OXFORD. [*Received, November 3rd*, 1925.]

The Effect of Heat on Chloral Hydrate. By JAMES DENIS MOUNFIELD and JOHN KERFOOT WOOD.

THE temperature at which the dissociation of chloral hydrate commences is unknown. It is complete at 78°, and the variability of the melting point suggests that it may occur to a considerable extent at about 50°. Pope (J., 1899, **75**, 455) has suggested that two modifications of chloral hydrate may exist, but the work of Van Rossem and Jaeger (*Z. physikal. Chem.*, 1908, **62**, 701) would appear to discredit this view.

To obtain further information on these matters, the authors have conducted dilatometric and tensimetric measurements with chloral hydrate. Repeated experiments with "liquid paraffin B.P." as the indicating liquid showed that chloral hydrate suffers a change of volume at 32°; similar indications were given by samples which had been maintained at 20° and 40° for several days and which were slowly heated and cooled, respectively.

In the tensimeter experiments, the vapour pressure was measured at small intervals of temperature between 15° and 40°. The results are in Tables I and II, the former referring to rising and the

latter to falling temperature; the pressures indicate millimetres of α-bromonaphthalene.

TABLE I.

Temp.	Press.	Temp.	Press.
15·65°	6·12	31·10°	17·29
18·90	8·16	31·90	18·08
19·80	8·67	33·00	19·33
21·30	9·53	34·00	20·31
23·01	10·69	34·55	21·20
24·80	11·96	35·50	22·38
26·70	13·40	36·50	23·95
27·10	13·78	37·30	24·82
28·50	14·99	37·73	25·34
29·50	15·90	38·05	26·20
30·35	16·63	38·50	26·90

TABLE II.

Temp.	Press.	Temp.	Press.
37·70°	25·29	30·00°	16·20
37·25	24·60	28·70	15·22
36·43	23·61	27·60	14·08
35·90	22·72	25·70	12·59
34·95	21·70	24·00	11·20
33·60	19·80	21·80	10·00
32·50	18·60	20·85	9·21
31·50	17·81	19·45	8·42
31·20	17·56	—	—

The values obtained in the two series of experiments are in agreement and show the complete absence of a break in the vapour pressure curve in the vicinity of 32°; Ramsay and Young (*Phil. Trans.*, 1886, **177**, 76), from observations made at much larger intervals of temperature, also obtained a smooth curve. From the absence of a break in the vapour pressure curve it would appear most probable that the change which occurs at 32° does not correspond to a change of modification, but marks the commencement of the dissociation of chloral hydrate.—MUNICIPAL COLLEGE OF TECHNOLOGY, UNIVERSITY OF MANCHESTER. [*Received, October 10th*, 1925.]

Preparation of Ethylene Bromohydrin. By FREDERICK HENRY MCDOWALL.

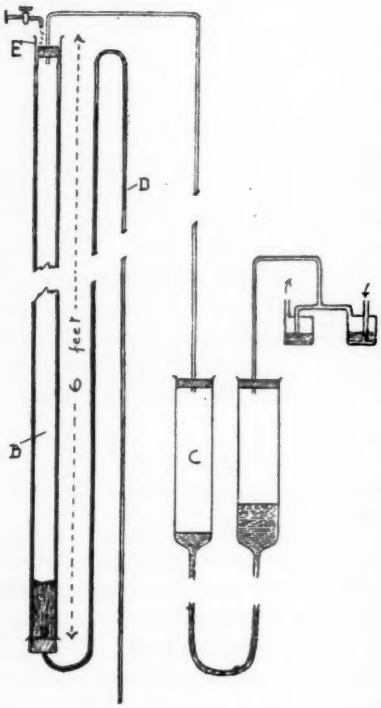
IN the method of preparation of ethylene bromohydrin described by Read and Williams (J., 1917, **111**, 240) and Read and Brook (J., 1920, **117**, 359, 1214), bromine is carried over into the reaction chamber in the form of vapour by a current of air. This has several disadvantages. The ethylene becomes considerably diluted by the air, and a great deal is carried away, so that of the total amount used, only one-third is absorbed. Furthermore, the supply of bromine is not easily regulated.

These disadvantages can be obviated by dropping the bromine from a small, finely-pointed burette down a guide-tube of small bore, the lower part of which reaches to the bottom of the reaction vessel, and is placed as far as possible from the ethylene inlet. The bromine can thus be introduced slowly and, with an efficient stirrer, it becomes dissolved in the water before contact with gaseous ethylene is possible. The yields obtained in two experiments coincided with the average of those obtained by Read and Brook

(*loc. cit.*, p. 1214), while the quantity of ethylene used was only slightly in excess of that absorbed. [*Received, January 12th,* 1926.]

An Automatic Siphonic Gas Circulator. By GEORGE M. GREEN.

THE apparatus described is the result of an unsuccessful attempt to construct a gas-circulating device of the type communicated by Pearson and Thomas (J., 1925, **127**, 2450). It does not contain a mechanical device of the plunger variety, and the advantages claimed for it are simplicity of construction and perfect continuity of action, once started. Its disadvantages lie in its comparative slowness and its well-defined intermittency. For certain kinds of laboratory work, however, the latter might recommend themselves.



The apparatus consists of two concentric glass tubes, *B* and *E*, about 6 feet long, one of which slides within the other, the annular space between them being about 1 mm. The inner tube, about 1 inch in internal diameter, is sufficiently heavy to resist the upward-moving tendency produced by the developing hydrostatic pressure. The siphon tube, the length of which can be varied by means of rubber tubing, should be of the greatest possible diameter consistent with rapid and efficient siphonage, and be placed at a suitable height above the working bench. The inflowing water, preferably under a constant pressure head, requires careful regulation at the commencement. The diameter of the upper portions of the U-tube, *C*, containing the oscillating mercury is 2 inches. The valves are of the ordinary mercury seal type. With this apparatus, a constant circulation of at least 50 c.c. of gas per minute is obtainable.—TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, December 28th,* 1925.]